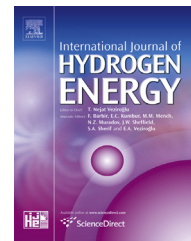


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Microwave synthesis & sintering of Sm and Ca co-doped ceria ceramics

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ABSTRACT

In this work we report on the combined use of microwave (MW) heating sources for the powder synthesis and the ceramic sintering of Sm and Ca co-doped ceria $\text{Ce}_{0.8}\text{Sm}_{0.18}\text{Ca}_{0.02}\text{O}_{1.9}$ polycrystalline materials for potential application as an electrolyte in intermediate-temperature solid oxide fuel cells (IT-SOFCs). We investigate the crystal structure, ceramic microstructure and the oxygen ion conductivity in detail and compare the latter to conventionally sintered ceramics. MW sintering of ceramic pellets leads to only slightly increased resistivity as compared to conventional sintering, but offers massive energy and time savings for potential industrial production processes. Exceptionally high oxygen ion conductivity without any significant electronic contribution was found in MW synthesized and MW sintered pellets, where the total resistivity, composed of grain boundary and bulk contributions, was found to be in the range of 0.5–1 kΩ at 500 °C. Sm- and Ca co-doped ceria may be well-suited for electrolyte materials in IT-SOFCs.

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Introduction

Solid oxide fuel cells (SOFCs) allow the electrochemical conversion of hydrogen and oxygen gases into electrical power and heat, and only H_2O remains as a by-product. Therefore, SOFCs constitute an environmentally friendly option to replace conventional engines based on fossil fuels with problematic CO_2 carbon emissions. The desired temperature

of operation of SOFCs depends on the application, where in the case of domestic use or in the automotive industry a reduced value is desired for practical reasons. Therefore, significant research effort is dedicated nowadays to reduce the operating temperature of current state-of-the-art SOFCs from 800–1000 °C to 500–800 °C in order to develop operational intermediate temperature SOFCs (IT-SOFCs) [1,2]. In addition to the reduced operating temperature, IT-SOFCs would be cheaper to fabricate, more rapid to start-up and shut-down,

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and exhibit reduced corrosion rate of metallic components and an improved durability.

The development of an appropriate electrolyte material with sufficiently high oxygen ion conductivity at lower operating temperatures is one of the major challenges to develop IT-SOFCs. An ideal electrolyte material for IT-SOFCs should have the following characteristics [3–7]:

- High ionic and negligible electronic conductivity at the operating temperature
- Good thermal and chemical stability in relation to the adjacent anode and cathode materials
- Low cost
- Environmentally benign material characteristics

A promising choice of electrolyte materials may be the system with the fluorite-type crystal structure and chemical formula AO_2 , which may be considered the archetype system for materials with high oxygen ion conductivity [8–12]. The unit cell is a face-centered cubic arrangement of tetravalent A-cations with oxygen anions occupying tetrahedral sites, leading to a large number of octahedral interstitial voids [13]. Thus, this structure may be regarded as a rather open one [14,15]. Doped ceria materials with the fluorite structure have been extensively studied as potential electrolytes in IT-SOFCs [16–20], where oxygen vacancies can be introduced into the system when Ce^{4+} cations are substituted by divalent alkaline and/or trivalent rare earth (RE) cations [21–24]. Ideally, the oxygen vacancies are randomly distributed throughout the oxide sublattice, which is an essential feature required for homogenous oxygen vacancy conduction. The highest conductivity is observed at the highest oxygen vacancy concentration when the aliovalent doping cation occurs in the highest concentration possible close to the solid-solution limit, and has an ionic radius (i.r.) close to that of the host cation. In the case of Ce^{4+} (i.r. = 0.097 nm), this may be Sm^{3+} (i.r. = 0.107 nm) or Gd^{3+} (i.r. = 0.105 nm) [1,14,22–25] [3,17,25–28]. It was recently shown that (i) Sm-doped ceria ceramics provide higher oxygen ion conductivity than Gd doped or Sm–Gd co-doped ceramics, and (ii) MW chemical synthesis leads to higher ionic conductivities in the sintered pellets as compared to conventional synthesis [29,30]. Furthermore, Moure et al. have demonstrated that the resistivity of the grain boundary (GB) areas can be reduced when RE-doped ceria are co-doped with a small quantity of Ca [30,31]. The reduction of the GB resistivity is in fact essential, because the GBs constitute barriers for the oxygen ion charge transport, although they may be relatively thin. The GB barriers are often described in the framework of a Schottky-type barrier model [32].

It had been shown previously that the synthesis of nanoparticles helps to achieve better ceramic sintering densification due to the increased sintering activity of high surface area powders [19,20,33], which then leads to reduced GB resistivity. In this context, microwave-hydrothermal synthesis has emerged as a time and energy efficient technique to produce nanosized ceria-based powders for IT-SOFC applications [34–37].

Furthermore, the option to extend the use of microwave (MW) radiation as a heat source to the sintering process of

ceramics has recently appeared as an additional interesting possibility to further reduce energy and time consumption in environmentally friendly ceramic processing technology [38–42]. The MW sintering process works equivalent to the synthesis, where heat is generated internally in the reactants or the pressed green pellets through the interaction of the MWs on a microscopic level with atoms, ions and dipoles in the material. This produces an inverse heating profile as compared to the conventional heat transfer by heat convection, i.e. in MW heating processes the material is heated directly “from inside”. By switching on the microwave radiation source, the interior areas of the sample will be heated first but the heating profile becomes more uniform after few seconds of MW irradiation and the outer areas will be heated as well [43].

In the present work, microwave-hydrothermal nanopowder synthesis and single-mode MW ceramic sintering as well as conventional sintering of optimally doped $\text{Ce}_{0.8}\text{Sm}_{0.18}\text{Ca}_{0.02}\text{O}_{1.9}$ materials are studied in detail, including structural and microstructural characterization, and ionic conductivity measurements of the resulting ceramic pellets. Throughout this work it was intended to utilize all possible means to reduce the GB barrier resistivity as much as possible to optimize the overall ionic conductivity:

- (a) Synthesizing nanopowders with increased sintering activity using MW heating
- (b) Use the preferred Sm cation for RE-doping
- (c) Apply additional Ca doping to a small extent

By following this strategy we obtain ceramics with oxygen ion conductivities that are among the highest values reported so far in ceramic oxygen ion conductors [30]. Therefore, MW synthesized and MW sintered $\text{Ce}_{0.8}\text{Sm}_{0.18}\text{Ca}_{0.02}\text{O}_{1.9}$ ceramics may be strong candidates for the use as electrolyte materials in IT-SOFCs.

Experimental procedure

Synthesis

The synthetic procedure for $\text{Ce}_{0.8}\text{Sm}_{0.18}\text{Ca}_{0.02}\text{O}_{1.9}$ is equivalent to the one described previously in Ref. [26] for different RE-doped ceria. Here, the starting chemicals were Cerium (III) nitrate hexahydrate $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\geq 99\%$ (Sigma–Aldrich), Samarium (III) nitrate hexahydrate $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.9% (Sigma–Aldrich), Calcium (II) nitrate tetrahydrate $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\geq 99\%$ (Sigma–Aldrich) and Potassium hydroxide KOH flakes, 90% (Sigma–Aldrich). Aqueous solutions were prepared by dissolving the nitrate salt in the desired ratios in distilled water and 1.2 M KOH under constant stirring. In a typical experiment ≈ 40 ml solution was produced, which was then ultrasonically dispersed for 2 min. The synthesis reactions were carried out in double-walled vessels consisting of an inner Teflon sealed autoclave and an outer shell of high strength polymer. The double-walled vessels were placed in a commercial Milestone ETHOS 1 microwave system, which was operated at 2.45 GHz and was equipped with a stirring motor. The heating ramp up to 200 °C was ≈ 10 °C/min and the

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