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Chemical stability and electrical properties of Nb doped $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ as a high temperature proton conducting electrolyte for IT-SOFC

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Abstract

$BaCe_{0.9-x}Nb_xY_{0.1}O_{3-\delta}$ (where $x=0$, 0.01, 0.03 and 0.05) powders were synthesized by solid-state reaction to investigate the influence of Nb concentration on chemical stability and electrical properties of the sintered samples. The dense electrolyte pellets were formed from the powders after being uniaxially pressed and sintered at 1550 °C. The electrical conductivities determined by impedance measurements in temperature range of 550–750 °C in different atmospheres (dry argon and wet hydrogen) showed a decreasing trend with an increase of Nb content. For all samples higher conductivities were observed in the wet hydrogen than in dry argon atmosphere. The chemical stability was enhanced with increasing of Nb concentration. It was found that $BaCe_{0.87}Nb_{0.03}Y_{0.1}O_{3-\delta}$ is the optimal composition that satisfies the opposite demands for electrical conductivity and chemical stability, reaching 0.8×10^{-2} S cm^{-1} in wet hydrogen at 650 °C compared to 1.01×10^{-2} S cm^{-1} for undoped electrolyte.

Keywords: C. Ionic conductivity; D. Perovskites; E. Fuel cells

1. Introduction

Materials with perovskite structure based on barium cerate ($BaCeO_3$) have been widely investigated as electrolytes for intermediate-temperature solid oxide fuel cells (IT-SOFC). They expose proton conductivity when Ce^{4+} is substituted with small amounts of aliovalent cations such as Y^{3+}, In^{3+} and other rare earth cations (Gd^{3+}, Sm^{3+}, etc.) [1–6]. These cations cause the formation of point microstructure defects, i.e. oxygen ion vacancies (1) that further react with hydrogen, (2) or water vapor and (3) according to the following mechanism using Kröger–Vink notation [3,7,8]:

$$CeCe^x + 1/2O_O^x + 1/2M_2O_{3(s)} \rightarrow MCe' + 1/2V_O^{\bullet\bullet} + CeO_{2(s)} \quad (1)$$

$$H_{2(g)} + V_O^{\bullet\bullet} + 2O_O^x \leftrightarrow 2OH_O^{\bullet} \quad (2)$$

$$H_2O_{(g)} + V_O^{\bullet\bullet} + O_O^x \leftrightarrow 2OH_O^{\bullet} \quad (3)$$

The transport process of protons can be described by Grotthuss mechanism, where a relatively small activation energy is necessary (0.4–0.7 eV) for a proton to hop from one oxygen ion site to adjacent one. The reactions (2) and (3) were shown to be exothermal [9], which means that the proton conduction is dominant at lower temperatures, while at higher temperatures the reaction equilibrium is shifted towards the formation of oxygen vacancies, thus favouring a conducting mechanism that involves oxygen ions.

However, compared to oxygen-ion conductors, the protonic ones expose higher conductivities at lower temperatures, allowing SOFCs to be made of cheaper materials, which in addition to lower operating temperatures will reduce the overall costs of their usage. The another advantage of the proton conducting SOFCs is that water vapor, as the product of the electrochemical reaction, emanates at the cathode site, thus preventing dilution of the fuel fed at the anode site, which is the case in the oxide-ion conducting SOFCs [10,11].

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Despite its high conductivity has been challenged by recent investigations [6], $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ (BCY10) is recognized as one of the best perovskite-based proton conductors.

On the other hand, the main drawback of BCY10 is its chemical stability. The presence of CO_2 and water vapor at raised temperatures extensively deteriorate its microstructure, negatively affecting the electrical properties and durability of SOFCs [12,13]. Many investigations have been done on how to improve the chemical stability of barium cerates, all of which could be roughly divided into two main approaches. The first is to make solid solutions of barium cerates and more stable barium zirconates [14,15] and the second is co-doping B-sites with various cations such as Nb or Zr that would provide good stability [16–18]. Yet, it is normal to expect lower conductivities on account of chemical stability and other way round, which implies defining the optimal solution as a chemically stable system without significantly reduced conductivity.

It has been previously reported [18] that amounts of 0.03–0.12 mol% Nb^{5+} can secure satisfactory stability, but with solemn decline of electrical properties. The aim of this work is to investigate the influence of lower concentrations of Nb^{5+} (up to 0.05 mol%) on chemical stability and electrical properties of BCY10 and to determine the optimal concentration of Nb in BCY10 that will provide chemically stable microstructure with good electrical conductivity.

2. Experimental

2.1. Synthesis of the ceramic powders by solid-state reaction (SSR) method

$BaCe_{0.9-x}Nb_xY_{0.1}O_{3-\delta}$ (BCNY) powders (where $x=0$, 0.01, 0.03 and 0.05), denoted as BCY10, BCNY001, BCNY003 and BCNY005, were synthesized by the method of solid state reaction. Barium(II)-carbonate (Merck, 99%), cerium(IV)-oxide (Carlo Erba), yttrium(III)-oxide (Merck) and niobium(V)-oxide were homogenized with isopropyl-alcohol for 24 h in a planetary ball mill using tungsten carbide jar and balls. The mixture was dried at 50 °C for 2 h and ground in an agate mortar. Then the powders were fired at 1000 °C for 5 h to initiate the solid state reaction. Since the XRD patterns proved the existence of single BCNY phase, the powders were ground again, sieved through a 75 μm mesh, uniaxially pressed before sintering at 1550 °C for 5 h.

2.2. Characterization

The characterization of the powders was performed by differential scanning calorimetry-thermogravimetric (DSC-TGA) analysis (SDT Q600 V7.0 Build 84) and X-ray diffraction (XRD) analysis. The microstructure of the sintered pellets was also investigated by scanning electron microscopy (SEM) (TESCAN Vega TS5130MM) and XRD analysis.

Electrical characterization was performed on Pt/BCNY/Pt symmetrical cells within temperature range of 550–750 °C in wet H_2 (3 vol% H_2O) and in dry Ar atmosphere. This temperature range was chosen because it is the range of working temperatures for IT-SOFCs. The samples were prepared for electrical measurements by applying a thin Pt-paste layer on both sides of the pellets. The pellets with Pt-paste had been dried at 100 °C for 2 h before being treated for 30 min at 750 °C. Electrochemical impedance spectroscopy (EIS) was performed using a HIOKI 3532-50 LCR HiTESTER in a frequency range between 42 Hz and 1 MHz. The wet hydrogen atmosphere was provided by letting the gas through a gas washer filled with distilled water at the room temperature. In the other case, to secure dry argon medium the gas was passing through a gas trap filled with P_2O_5 prior to entering the aperture. In both cases the flow rate of the gases through the system was kept at 50 cm^3/min using a digital mass flow controller and meter (MKS PR 4000B-F).

2.3. Chemical stability

The sintered pellets were exposed to CO_2 atmosphere at 700 °C for 5 h by keeping the flow rate of CO_2 through the aperture at 400 cm^3/min. After being exposed the pellets were investigated by the XRD analysis in order to determine the changes in their microstructure.

3. Results and discussion

3.1. DSC-TGA analysis and X-ray diffraction patterns

In order to find out optimal processing conditions for synthesis of BCNY powders by the SSR method, it is suitable to start from the results of the DSC-TGA analysis. In Fig. 1 the DSC-TGA analysis of BCNY003 powder is shown. The first endothermic peak on the heat flow curve indicates the transformation from an orthorombic α-$BaCO_3$ phase to a trigonal, β-$BaCO_3$ phase at 811 °C

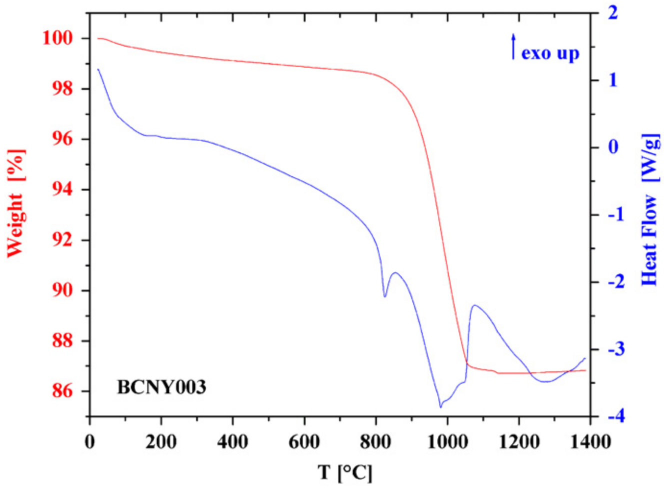

Fig. 1. DSC-TGA analysis of BCNY003 powder.