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Improved ceramic and electrical properties of $CaZrO_3$-based proton-conducting materials prepared by a new convenient combustion synthesis method

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ABSTRACT

The present work emphasizes the features of a new combustion synthesis method suitable for easy synthesis and sintering of $CaZrO_3$-based materials as promising proton-conducting electrolytes for electrochemical applications in solid oxide electrochemical devices. Sc- and In-doped $CaZrO_3$ compounds are selected to be the objects of investigation and their crystal structure properties as well as microstructural, thermal and electrical characteristics are studied by the means of X-ray diffraction analysis, high-temperature dilatometry, scanning electron spectroscopy, impedance and 4-probe DC conductivity techniques. The established properties are critically compared with previously obtained data to confirm the prospects of the proposed method synthesis for the preparation of Zr-based proton-conducting ceramic materials. It is found that $CaZr_{0.95}Sc_{0.05}O_{3-\delta}$ exhibits predominantly protonic conductivity under wet air atmospheres below 700 °C; while, $CaZr_{0.9}In_{0.1}O_{3-\delta}$ demonstrates a certain value of electronic conductivity along with ionic one.

1. Introduction

Perovskite-structured complex oxides based on $CaZrO_3$ are considered as promising functional ceramic materials for high-temperature applications, since 1991 when Iwahara and his co-workers have shown their successful employment in hydrogen sensors [1–3]. Heightened interest in this system is explained by the presence of higher contribution of proton conductivity as compared with other high-temperature proton-conducting materials with a perovskite structure ($SrCeO_3$, $BaCeO_3$, $SrZrO_3$, $BaZrO_3$) [4,5]. More precisely, doped $CaZrO_3$ can exhibit purely protonic transport in reducing atmospheres and predominantly protonic transport in wet oxidizing ones below 600 °C [6–8], while other representatives also demonstrate a meaningful level of oxygen-ionic or electronic conductivity at the same conditions. Such peculiar features can be explained by the fact that a decrease in A^{2+} ionic radius in ABO_3 perovskites (A=Ca, Sr, Ba and B=Ce, Zr) results in oxygen transport difficulties due to smaller cells volume, whereas the dimension and energetic characteristics of crystals affect the proton transport in a lesser degree [9,10]. In addition, zirconates along with excellent mechanical properties also possess relatively higher chemical stability against CO_2 in comparison with cerates of alkaline-earth elements [4]. This makes $CaZrO_3$ a suitable model system from the viewpoint of theoretical (modeling of the proton transport in oxide materials [11,12]) and applied (use sensors and solid oxide fuel cells [13–16]) aspects.

One of the important directions for successful electrochemical applications of $CaZrO_3$ materials is the optimization of their synthesis and sintering procedures as a strategy considerably affecting the structural and microstructural parameters and, correspondingly, related functional properties. Discussing in details, different synthesis techniques have been used to achieve single-phase and microstructurally quality ceramic materials, such as solid state reaction [6,17], co-precipitation [18,19], sol-gel [20,21], combustion synthesis [22,23], hydrothermal [24,25] methods e.t.c. It should be noted that the use of the solid-state reaction is concerned with high sintering temperatures (up to 1800 °C [17]) required for the desirable materials densification; at the same time, even the use of wet-chemical techniques does not guarantee the formation of dense and non-porous ceramics at lower sintering temperatures [20,22].

In the present work, we proposed a new combustion synthesis

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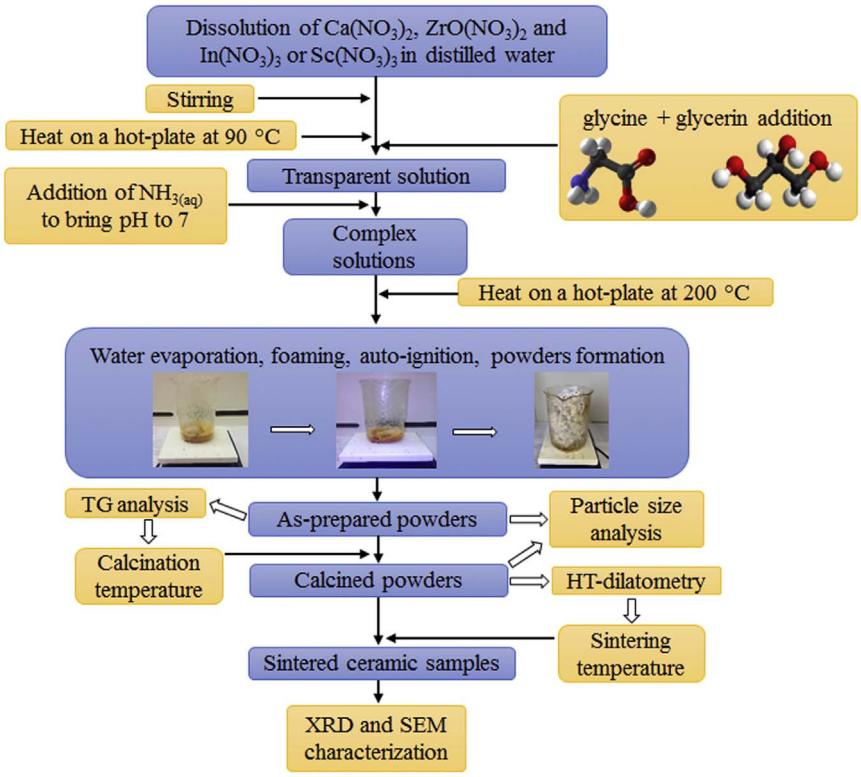

Fig. 1. A flow-chart of ceramic materials preparation.

method and carried out an in-depth investigation concerning the identification of correlations in the $CaZrO_3$ system between chemical composition, structure characteristics and functional properties. A glycine-glycerin-nitrate combustion synthesis method was proposed to obtain ceramic samples of the $CaZr_{0.95}Sc_{0.05}O_{3-\delta}$ and $CaZr_{0.9}In_{0.1}O_{3-\delta}$ compositions. The choice of selected compositions was caused by their wide and thorough investigations. This allows us to carry out the comparative analysis between the developed method and recently proposed ones. Moreover, In and Sc dopants differently affect the properties because the addition of indium (in contrast with scandium) facilitates the densification of materials. Therefore, the proposed method can be used not only for quite easy sinterable, but also for more refractory material.

2. Experimental

2.1. Details of materials preparation

The materials with the $CaZr_{0.95}Sc_{0.05}O_{3-\delta}$ (CZS) and $CaZr_{0.9}In_{0.05}O_{3-\delta}$ (CZI) compositions were prepared by a glycine-glycerin-nitrate combustion synthesis method (Fig. 1). The combination of two organic substances as a fuel was caused by good complexation of glycine with metal cations and required polymerization properties of glycerin [26,27].

The $Ca(NO_3)_2$, $Sc(NO_3)_3$, $In(NO_3)_3$ nitrates and $ZrO(NO_3)_2$ oxynitrate (in hydrate forms, purity not less than 99.5%) were completely dissolved in a distilled water under thorough stirring at 90 °C. Then complexing (C) and polymerizing (P) agents were added to the total metal-ions (M) in the following mole ratio: C:P:M=1:0.5:1. After a transparent solution was obtained, ammonia solution was drop-by-drop added in order to change the pH level of the solution from acidic to neutral condition that prevents the salts precipitation under further evaporation. The obtained solution was then heated up to 200 °C, when the stages of water evaporation, intensive foaming and auto-ignition were consequentially observed. The as-obtained gray-colored powders were calcined at 700 °C for 1 h to remove carbon and organic-containing residues and then at 950 °C for 5 h for $CaCO_3$ decomposition and preliminary solid solution phase formation.

The value of calcination temperature was selected on the base of thermogravimetric analysis. This analysis was carried out between 20 and 1000 °C in air atmosphere using a synchronous thermal analyzer STA 449F1 Jupiter® coupled with a quadrupole mass spectrometer QMS 403C Aëolos.

The powders were qualitatively investigated by BET method using a SORBI 4.1 analyzer to evaluate the characteristic size parameters of the combusted powders and propensity to agglomeration of the calcined ones. Then the powders were uniaxally pressed at 200 MPa and sintered at a temperature, which was chosen on the base of high-temperature dilatometry data. The dilatometry measurements were carried out by the means of a NETZSCH DIL 402 C dilatometer to evaluate the optimal sintering temperature. The experimental conditions were as follows: air atmosphere, heating up to 1550 °C, heating/cooling rates of 3 °C min^{-1}.

2.2. Materials characterization

The sintered ceramic materials were examined by X-ray diffraction (XRD) using $CuK_{\alpha 1}$ radiation monochromatized by Si-monocrystal at room temperature in ambient air (RIGAKU D/MAX-2200). The scans ranged between $15° \le 2\theta \le 75°$ with a scan rate of 2° min^{-1}. The structural refinements were analyzed using a Fullprof software [28].

The morphology of the sintered materials was investigated by scanning electron microscopy (SEM, JEOL JSM-5900 LV).

The thermal behavior of ceramic samples was evaluated using the dilatometry analysis, the features of which were described above. The thermal expansion coefficient (TEC) values were calculated on the basis of dilatometry dependences obtained within a temperature range of 50–1000 °C.

AC impedance measurements were carried out over a frequency range of $5 \cdot 10^2$–$1 \cdot 10^6$ Hz (an Ellins Z-1000P Frequency Response Analyzer, Chernogolovka, RF). Calculations of the resistance were carried out using the Zview software fitting. All the electrochemical