Regular Article

Scandia stabilized zirconia-ceria solid electrolyte (xSc1CeSZ, 5 < x < 11) for IT-SOFCs: Structure and conductivity studies

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ARTICLE INFO

ABSTRACT

The current study looks at Sc_2O_3 (5–11 mol%) stabilized ZrO_2-CeO_2 solid electrolyte for application in IT-SOFCs. Using XRD, Raman spectroscopy, and impedance spectroscopy, it was found that the addition of 1 mol% CeO_2 in the ZrO_2 host-lattice increases the tendency to form high-symmetry, high-conductivity phases at the expense of low-symmetry, low-conductivity phases, resulting in higher total ionic conductivity. Moreover, the conductivity maximum has broadened and shifted to lower Sc_2O_3 content. The phase equilibria and conductivity results are explained on the basis of larger ionic size of Ce^{4+}, which enforces higher symmetry as evidenced by lower axial ratio (c/a) in tetragonal phase.

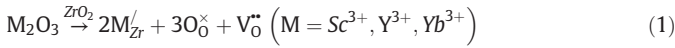© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Lowering the high operating temperature (~1000 °C) of solid oxide fuel cells (SOFCs) to intermediate temperature (IT) range (500–700 °C) can significantly improve their durability, reduce their cost of fabrication, and, more importantly, expand their applicability to portable power and transportation markets [1]. Scandia stabilized zirconia (ScSZ) possesses significantly higher oxygen-ion conductivity than the state-of-the art 8 mol% yttria-stabilized zirconia (8YSZ) and, therefore, opens up the possibility to reduce the operational temperature of SOFCs. E.g. at 850 °C, 11 mol% ScSZ (11ScSZ) has an ionic conductivity of 108 mS/cm, which is >30% higher than that of 8YSZ (78 mS/cm) [2]. However in the intermediate temperature range, the conductivity of 11ScSZ decreases significantly due to the transformation of highly conductive, disordered, cubic fluorite phase to low conductive, ordered, rhombohedral β-phase [3]. The present work looks at ZrO_2-CeO_2 stabilized with Sc_2O_3 in low-concentration range (5–11 mol%) as a candidate electrolyte for IT-SOFCs. Further, the understanding of structure-conductivity correlations in these compositions is also relevant for application in three-way catalysts, solar thermochemical fuel production and micro solid oxide fuel cell operating at low temperatures. [4–6].

The phase chemistry of ZrO_2-R_2O_3 (R = Y, Sc, Er) is highly complex and Yashima et al. [7] have noted that phase equilibrium is difficult to achieve below 1200 °C, due to slow kinetics of diffusional transformations and of cation-diffusion less transformations, leading to the formation of several metastable phases. Similar ionic radii of the host ($r^{4+}_{Zr,VIII} = 0.84$ Å) and dopant ($r^{3+}_{Sc,VIII} = 0.87$ Å) in ZrO_2-Sc_2O_3 system contribute further to the slow kinetics [8]. In the compositional range of interest for the present study, monoclinic (m), tetragonal (t), cubic (c), metastable tetragonal (t′ and t″), and metastable rhombohedral β ($Sc_2Zr_7O_{11}$) phases are known to exist [7]. With respect to electrical conductivity, cubic fluorite and tetragonal are the most desirable phases. Badwal et al. [9] studied the phase chemistry and ionic conductivity of ZrO_2-Sc_2O_3 system between 7 and 11 mol% Sc_2O_3 and found that the cubic phase at 9.3 mol% shows an ionic conductivity of the highest magnitude and temporal stability. At 7–9 mol% Sc_2O_3, the phase composition consists of t′-phase whose conductivity decays with annealing as the metastable phase decomposes into Sc-rich cubic matrix and fine precipitates of Sc-deficient tetragonal phase with low conductivity. At 10–11 mol% Sc_2O_3, the phase composition consists of cubic and β-phase which results in - 1) hysteresis in conductivity during heating and cooling cycles due to slow transformation kinetics between cubic and β-phase and 2) a step in Arrhenius plot of conductivity at ~600 °C due to the significantly lower conductivity of β-phase. Moreover at high Sc_2O_3 dopant level, high vacancy concentration results in the formation of ordered phases over long annealing periods resulting in conductivity decay, albeit slower than that observed for t′-phase.

Within the ZrO_2-Sc_2O_3 system, second dopant (Y^{3+}, Yb^{3+}, Ga^{3+}, Hf^{4+}, Ce^{4+}) has been studied to improve phase stability of cubic phase and to improve conductivity [3,10–12]. At small doping levels (<2 mol%), the second dopant stabilizes the cubic phase over β-phase, possibly due to the lattice strains generated by the second dopant, and results in a linear Arrhenius plot of conductivity versus temperature, without a step, and in a higher conductivity at intermediate temperatures. The correlations between the lattice strain and oxygen-ion conductivity in fluorite-structured oxides have been well studied [4, 13–16]. Recently, the beneficial effect of tuning lattice strain on the phase stabilization of δ-Bi_2O_3 and consequently on the enhancement of ionic conductivity has been reported by Pryds et al. [17].

Unlike trivalent-dopant oxides, CeO_2 exists in the desired cubic fluorite structure and alloying of CeO_2 into ZrO_2 does not create additional oxygen ion vacancies as expressed in the Kröger-Vink notation below.

$$M_2O_3 \xrightarrow{ZrO_2} 2M'_{Zr} + 3O_O^{\times} + V_O^{\bullet\bullet} \left(M = Sc^{3+}, Y^{3+}, Yb^{3+} \right) \tag{1}$$

$$CeO_2 \xrightarrow{ZrO_2} Ce_{Zr}^{\times} + 2O_O^{\times} \tag{2}$$

Further, higher ionic radius of Ce^{4+} ($r_{Ce,VIII}^{4+} = 0.97$ Å) compared to that of host promotes oxygen vacancies to reside next to the host cations, rendering stability to the cubic fluorite structure and reducing the tendency to transform into low-symmetry phases [12]. Therefore, CeO_2 should be considered as a phase stabilizer in the ZrO_2 host lattice, rather than as a dopant in the traditional sense to increase the concentration of ionic defects. As earlier studies [3,11,18] looked at xSc_2O_3-$1CeO_2$-$(99-x)ZrO_2$ ($xSc1CeSZ$) system at high Sc_2O_3 dopant level ($x \geq 10$ mol%), this work intends to extend the analysis of this system to lower Sc_2O_3 dopant levels ($x = 5$–11 mol%) with respect to phase structure and ionic conductivity. The current work has relevance for IT-SOFCs from three perspectives - 1) Higher level of doping concentration (≥ 10 mol% Sc_2O_3) results in the formation of local defect structures in these oxides which trap oxygen vacancies and reduce ionic conductivity [1], 2) Cost of Sc_2O_3 is >10 times that of CeO_2 and ZrO_2 and lower Sc_2O_3 doping level would reduce the cost of ScSZ based SOFCs [2], and 3) tetragonal phase (e.g. 6Sc1CeSZ) is mechanically stronger than cubic phase (e.g. 10Sc1CeSZ) for electrolyte supported cells [19].

2. Experimental

Polycrystalline samples of $xSc1CeSZ$ ($x = 5$–11) were made by solid-state method starting with Sc_2O_3 (99.9% purity, Alfa Aesar), CeO_2 (99.99% purity, Alfa Aesar), and ZrO_2 (99% purity, Samics Research Materials Pvt. Ltd., India) powders. For comparison, samples of 9ScSZ and 11ScSZ were also fabricated under similar conditions. The stoichiometry of synthesized compositions and their corresponding nomenclature are given in Table 1. The stoichiometric amounts of powders were weighed and ball milled using zirconia ball media for 24 h in ethanol with 2 wt.% ammonium polyacrylate as a dispersant. The ball-milled ceramic slurries were dried at 100 °C overnight followed by calcination at 1350 °C for 6 h. The obtained powders were pressed into disk-shaped pellets and were sintered at 1550 °C for 10 h. The density values ranged from

4.95 to 5.25 g/cm³, with the relative theoretical density around 90% in all the samples. The crystalline phases present in polished sintered pellets were identified at room temperature using a laboratory X-ray diffractometer (Bruker D-8 focus with 1D lynxeye detector, Karlsruhe, Germany) with CuK_α incident radiation in 2θ range from 20 to 80°. Phases present in XRD pattern of each composition were initially identified, and subsequently, lattice parameters of all the observed phases were refined by whole pattern fitting method using TOPAS software. For the analysis, standard powder diffraction cards (Joint Committee on Powder Diffraction Standards) with the reference code of 01-089-5474, 01-089-5481, and 01-089-5485 were used for monoclinic, tetragonal, and cubic zirconia phases, respectively.

Phases revealed by XRD analysis were verified by performing Raman spectroscopy on sintered pellets between 200 and 1000 cm⁻¹ using a Raman system (Princeton Instruments, Acton spectrapro® SP-2500) with a polarized He-Ne laser ($\lambda = 633$ nm) at 80 mW. Impedance spectroscopy technique was used to evaluate the ionic conductivity of the polycrystalline ceramic samples as a function of temperature in air. For the measurements, Pt paste (Siltech Corporation, Bengaluru, India) was brushed onto both faces of the polished disk-shaped pellet to serve as the electrode and fired at 900 °C for 1 h in air. The impedance of the sample was measured at 250–700 °C in air using impedance analyzer (Solartron 1260 A, UK) over the frequency range from 32 MHz to 0.1 Hz with an applied amplitude of 50 mV.

3. Results and discussion

XRD patterns of sintered pellets revealed that at low Sc-doping levels (i.e., 5Sc1CeSZ and 7Sc1CeSZ), both tetragonal and monoclinic (minority) phases were present (see Supplementary Fig. 1). At higher doping levels, Sc_2O_3 addition successfully stabilized a single-phase composition in the host crystal lattice of ZrO_2-CeO_2. The minority monoclinic phase completely disappeared at 8Sc1CeSZ resulting in a pure tetragonal phase. Further increase in Sc_2O_3 doping resulted in the stabilization of a single cubic phase at 9Sc1CeSZ and 11Sc1CeSZ. While in the ZrO_2-Sc_2O_3 system, 9ScSZ showed a single cubic phase and 11ScSZ contained a slight amount of β-rhombohedral phase along with the majority cubic phase. Phase analysis results are summarized in Table 1.

Fig. 1 shows the estimated unit cell parameters for the majority phase observed in $xSc1CeSZ$ ($x = 5$–11). The unit cell parameters of the tetragonal phase in $xSc1CeSZ$ ($x = 5$–8 mol%) vary anisotropically with Sc_2O_3, as also observed for the tetragonal phase in $xScSZ$ system by Fujimori et al. [20] (shown in Fig. 1). With an increase in x, the lattice parameter a_t of tetragonal phase remains almost constant, while the other parameter c_t declines and approaches the value of $\sqrt{2}a_t$ in both $xSc1CeSZ$ and $xScSZ$ systems. However, the value of $\sqrt{2}a_t$ is higher and c_t is lower for the tetragonal phase in $xSc1CeSZ$ compared to that in $xScSZ$. The lower c_t/a_t ratio of tetragonal phase in $xSc1CeSZ$ clearly indicates that the addition of CeO_2 in ScSZ reduces the asymmetry of the tetragonal phase in low Sc_2O_3 containing compositions. The unit cell parameters of cubic phase existing in 9Sc1CeSZ, 11Sc1CeSZ, 9ScSZ, and 11ScSZ are also presented. The lattice parameter of $xSc1CeSZ$ in cubic phase is higher than that of $xScSZ$ due to the larger size of

Table 1
Phase analysis of $xSc1CeSZ$ ($x = 5$–11), 9ScSZ, and 11ScSZ using XRD and Raman spectroscopy. Notations: m-monoclinic, t-tetragonal, t′-metastable tetragonal, c-cubic, and β-rhombohedral. [] denotes minority phase.

Nomenclature	Oxide composition	Stoichiometry	XRD analysis	Raman analysis
5Sc1CeSZ	$(Sc_2O_3)_{0.052}(CeO_2)_{0.011}(ZrO_2)_{0.937}$	$Sc_{0.10}Ce_{0.01}Zr_{0.89}O_{2-\delta}$	t + [m]	t
7Sc1CeSZ	$(Sc_2O_3)_{0.070}(CeO_2)_{0.011}(ZrO_2)_{0.919}$	$Sc_{0.13}Ce_{0.01}Zr_{0.86}O_{2-\delta}$	t + [m]	t
8Sc1CeSZ	$(Sc_2O_3)_{0.081}(CeO_2)_{0.011}(ZrO_2)_{0.908}$	$Sc_{0.15}Ce_{0.01}Zr_{0.84}O_{2-\delta}$	t	t + [t′]
9Sc1CeSZ	$(Sc_2O_3)_{0.093}(CeO_2)_{0.011}(ZrO_2)_{0.896}$	$Sc_{0.17}Ce_{0.01}Zr_{0.82}O_{2-\delta}$	c	c
11Sc1CeSZ	$(Sc_2O_3)_{0.111}(CeO_2)_{0.011}(ZrO_2)_{0.878}$	$Sc_{0.20}Ce_{0.01}Zr_{0.79}O_{2-\delta}$	c	c
9ScSZ	$(Sc_2O_3)_{0.09}(ZrO_2)_{0.91}$	$Sc_{0.165}Zr_{0.835}O_{2-\delta}$	c	c + [t′]
11ScSZ	$(Sc_2O_3)_{0.11}(ZrO_2)_{0.89}$	$Sc_{0.198}Zr_{0.802}O_{2-\delta}$	c + [β]	c + [β]