



Conductivity ageing studies on 1M10ScSZ ($M^{4+} = \text{Ce, Hf}$)

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ABSTRACT

The long-term conductivity stability is tested on zirconia based electrolyte materials for solid oxide fuel cell applications. The ageing studies have been performed on the samples of ZrO_2 co-doped with 10 mol% of Sc_2O_3 and 1 mol% MO_2 , where $M = \text{Ce}$ or Hf (denoted respectively 1Ce10ScSZ and 1Hf10ScSZ) in oxidising and reducing atmospheres, at 600 °C for 3000 h. At 600 °C, these compositions show initial conductivity of around 9–12 $\text{mS}\cdot\text{cm}^{-1}$ in air. After 3000 h of ageing, no phase transitions are observed in any of the samples. For the first 1000 h, the degradation rate is higher than in the subsequent 2000 h; thereafter, conductivity degrades linearly with time for all samples. In air, the loss in the conductivity is lower than in reducing conditions. The 1Ce10ScSZ shows the highest degradation rate of 3.8%/1000 h in wet H_2/N_2 after the first 1000 h of ageing. A colour change of the 1Ce10ScSZ sample from white to dark orange after ageing in reducing conditions indicates the reduction of Ce^{4+} cations. The high degradation rate in the 1Ce10ScSZ sample aged in reducing conditions is explained by the formation of Ce^{3+} cations. The colour gradient is observed within the sample suggestive of the slow reduction process in 1Ce10ScSZ. The inhomogeneous 1Ce10ScSZ sample is represented using a core–shell model, where the core is the unreduced portion inside the reduced shell. The model allows the conductivity of the reduced and aged shell to be determined from the total conductivity; this is also measured on a thin sample subjected to the similar ageing treatment. The conductivity behaviour upon re-oxidation of the samples aged in reducing conditions is also investigated in air at 600 °C for 2000 h. The observation of conductivity recovery in 1Ce10ScSZ supports our view that it is due to Ce re-oxidation. The Ce concentration across the grain boundary is also studied using transmission electron microscopy. No clear evidence of segregation was observed in 1Ce10ScSZ, possibly due to the low Ce content of the sample.

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1. Introduction

With high oxide-ion conductivity and low electronic conductivity, scandia stabilized zirconia (ScSZ) as an electrolyte offers an advantage of lowering the working temperature of solid oxide fuel cells (SOFCs) to intermediate temperature range (400–700 °C). It exhibits the highest ionic conductivity among the doped ZrO_2 systems [1]. At 850 °C, the ionic conductivity of ZrO_2 doped with 11 mol% Sc_2O_3 is nearly 50% higher than the state-of-the-art yttria stabilized zirconia [1]. Due to a recent fall in the price of Sc_2O_3 , the ScSZ system is gaining increasing interest for application in fuel cells and related electrochemical devices such as high-temperature water electrolyzers [2].

Pure ZrO_2 possess various phase transformations starting from the high-temperature cubic (c) phase to tetragonal (~2370 °C), and monoclinic (~1170 °C) [3]. These transformations are martensitic in nature and reverse during cooling. The high-temperature cubic or tetragonal phases of ZrO_2 can be stabilized at ambient temperature by doping with Sc^{3+} cations (Sc_{Zr}^{\prime}); this also leads to the formation of oxygen vacancies $V_{\text{O}}^{\bullet\bullet}$ as charge compensating defects. The vacancies

are mobile, leading to oxide-ion conductivity. The ionic conductivity increases with (Sc_{Zr}^{\prime}) doping level up to a point, but for Sc_2O_3 contents of 10 mol% or more, the c-phase transforms to the rhombohedral (β)-phase on cooling below 650 °C, with a concomitant drop in the conductivity [1,3,4]. The poor conductivity of the β -phase has been ascribed to $V_{\text{O}}^{\bullet\bullet}$ defect ordering at low temperatures [5]. The ordering also occurs over time at higher temperatures resulting in a phase transition from c to β -phase, which degrades the ionic conductivity. It has been reported that the $V_{\text{O}}^{\bullet\bullet}$ defect ordering can be suppressed by replacing slight amount of Sc_2O_3 with other oxides such as Al_2O_3 , Gd_2O_3 , Ga_2O_3 , Y_2O_3 , CeO_2 [5–9]. Although the co-dopant cations stabilize the c-phase to ambient temperature, a decrease in the conductivity is observed in all the co-doped ScSZ systems. Among various co-doped compositions reported in the literature, ZrO_2 co-doped with 1 mol% CeO_2 and 10 mol% Sc_2O_3 (1Ce10ScSZ) exhibits the highest conductivity (~16.7 $\text{mS}\cdot\text{cm}^{-1}$) at 600 °C [6]. Arachi et al. [8] have studied the structural behaviour of $((\text{ZrO}_2)_{1-x}(\text{CeO}_2)_x)_{0.89}$ (Sc_2O_3)_{0.11} and reported that the co-doped compositions (with CeO_2 content > 1%) no longer show an unfavourable phase transition at any temperature.

In addition to an initial high ionic conductivity for the electrolyte, minimal conductivity degradation at operating temperature is also essential: it has been stated that, for a viable SOFC, the conductivity

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degradation of the electrolyte should not exceed 0.1% over 1000 h [10]. Lee et al. [6] tested the stability of 1Ce10ScSZ at 1000 °C for 600 h in air. The stable conductivities obtained indicate no phase transition or other undesirable effects, such as grain boundary segregation and defect ordering. Stability tests also need to be performed at low temperatures, where the driving force for V_o° defect ordering is higher. With the expected lifetime of SOFCs exceeding 10,000 h, it is imperative to investigate the conductivity degradation for long times, and this should be done in both oxidising and reducing environments, corresponding to the cathode and anode compartments. Furthermore, Ce^{4+} is known to change its oxidation state to Ce^{3+} in reducing conditions, which may affect the structure and long-term conductivity stability of 1Ce10ScSZ. The present work explores this issue by studying the effects of annealing on the structure and conductivity of this material in both oxidising and reducing conditions at 600 °C for 3000 h. A parallel ageing study is performed on 10ScSZ doped with 1 mol% Hf^{4+} , which is a commonly found as impurity in ZrO_2 [2]. Further, as Hf^{4+} is a trivalent cation of stable valence, it provides a good comparison with the potentially reducible Ce^{4+} .

2. Experimental

Compositions with $1M^{4+}10ScSZ$ ($M^{4+} = Ce$ and Hf) were synthesized via conventional solid-state reaction method, starting from stoichiometric mixtures of 10ScSZ (99.99% purity from Seimi, Japan), CeO_2 (99.9% purity from Sigma Aldrich), and HfO_2 (99.9% purity from Sigma Aldrich) powders. All the starting powders were heated to 900 °C for 1 h in order to compensate for the loss on ignition. Accordingly, the stoichiometric amounts of powders were weighed and ball milled in ethanol for 24 h. The ball milled ceramic slurries were then dried at 100 °C. The agglomerated powders were ground using mortar and pestle and then uniaxially pressed into pellets and bars, followed by the isostatic pressing with 250 MPa for 1 min. The green products were then sintered in air at 1550 °C for 6 h, with the ramp rate of 100 °C/h for both heating and cooling. The relative geometrical density of the sintered ceramic samples was determined to be 96% of the theoretical density or above.

Ionic conductivity ageing studies were performed on the sintered ceramic samples of 1Ce10ScSZ and 1Hf10ScSZ using impedance spectroscopy at 600 °C. The samples were kept in air, and in a gas mixture of 9% H_2 , 1% H_2O and 90% N_2 (compositions in vol.%). The partial pressure of oxygen (PO_2), was determined using a Nernst sensor, was measured to be 5.1×10^{-26} atm. Pt paste (Ferro, type 64021015) was brushed onto both faces of the sintered pellet to serve as the electrode and fired at 1200 °C for 1 h in air. The impedance of the sample was measured in-situ using Solartron 1260 over the frequency range of 100 Hz to 2 MHz with an applied potential of 100 mV, at regular intervals, for a period of 3000 h. The grain and grain boundary resistance were obtained by fitting the observed impedance spectrum with the analog equivalent circuit $LR_g(R_{gb}Q_{gb})$ (R_eQ_e) where R_g , R_{gb} and R_e are the resistances due to grain, grain boundary and electrode respectively, and Q_{gb} and Q_e are the corresponding constant phase elements of the grain boundary and electrode, respectively. An inductance L was used in the equivalent circuit, to account for the effect of the leads which is apparent only at high frequencies. The conductivity behaviour was also studied upon re-oxidation of the samples aged in reducing conditions. The aged samples were kept in air at 600 °C for 2000 h, and in-situ impedance measurements were performed in regular intervals.

The scanning electron microscopy was performed using a Hitachi TM-1000 in backscattered mode, with the accelerating voltage of 15 kV. The sintered samples were mechanically polished to a mirror-finish using SiC abrasive discs of different grain size, followed by thermal etching. The clean polished surface of the samples was taken to the temperature of 1400 °C for 1 h with the ramp rate of 200 °C/h for both heating and cooling.

The chemical compositional analysis was performed using the transmission electron microscope (TEM, JEOL 3000FX) and electron dispersive spectroscopy (EDS) in scanning transmission electron microscopy (STEM) mode. For the TEM sample preparation, sintered disk of diameter ~3 mm and thickness ~20–30 μm was prepared using mechanical polishing via diamond lapping discs of different grades (Allied high tech products, Inc.). Using superglue, the thin sample was then mounted on the Cu TEM sample holder (with the shape of a ring). The sample placed on Cu sample holder was then further thinned in the low-angle ion-milling and polishing systems (Fischione instruments) with argon ions at an accelerating voltage of 5 kV, which were incident at both surfaces at an angle of 12–25° to yield an electron transparent specimen.

In order to study any phase transformation after the ageing period, X-ray diffraction (XRD) patterns were collected with Bruker D8 diffractometer (using the incident $CuK\alpha$ radiation) on both the aged and unaged sintered samples. Peak positions in the XRD pattern were determined by fitting each individual peak with a two symmetric Pearson VII profiles to model both $Cu K\alpha 1$ and $Cu K\alpha 2$ peak using commercially available software (i.e., Solver add-in within Microsoft Excel spreadsheet package). The lattice parameter was estimated using Nelson–Riley extrapolation method.

3. Results and discussion

3.1. Phase analysis

Fig. 1 shows the XRD profiles collected on the unaged and aged samples of 1Ce10ScSZ and 1Hf10ScSZ. The unaged sample of both the compositions exhibits cubic fluorite crystal structure, which confirms the stabilization of high-temperature c -phase to room temperature by the addition of 1 mol% co-dopant cations. The XRD profiles collected over the exposed surface of the aged samples look similar to that of the unaged samples. The residual peaks observed in the XRD profiles of the aged samples, correspond to Pt metal electrodes. In the inset of Fig. 1, the (220) diffraction peak of all the samples is shown. It can be seen that there are no extra diffraction peaks of β -phase present in the pattern. This indicates that no phase transition had taken place in 1Ce10ScSZ and 1Hf10ScSZ samples on ageing. Table 1 compares the lattice parameter for all the samples of 1Ce10ScSZ and 1Hf10ScSZ. The 1Ce10ScSZ sample shows lattice expansion during ageing in reducing conditions, which can be attributed to the reduction of Ce^{4+} cations to Ce^{3+} ($r^{3+}_{Ce,VIII} = 1.143 \text{ \AA}$, $r^{4+}_{Ce,VIII} = 0.970 \text{ \AA}$) [11]. The reason for the slight lattice expansion in the sample aged in air is not known. It may be associated with the homogenisation of the Ce^{4+} cations during the high-temperature ageing for a long duration. The lattice parameter of the unaged sample of 1Hf10ScSZ is lower than that of 1Ce10ScSZ, and is related to the smaller ionic radius of Hf^{4+} ($r^{4+}_{Hf,VIII} = 0.830 \text{ \AA}$). Further, the unaged and aged 1Hf10ScSZ samples show nearly the same lattice parameter which is to be expected, given the stable valence of Hf^{4+} even in reducing conditions.

3.2. Microstructural analysis

Fig. 2 shows the typical backscattered electron micrograph of a thermally etched unaged sample of 1Ce10ScSZ taken at the accelerating voltage of 15 kV. Microstructure looks quite dense with few residual isolated pores consistent with the obtained geometrical density of the sintered sample. The mean lineal intercept method was used to determine the average grain size. All the tested samples were similar in microstructure with the average grain size of around 10 μm . The unaged samples of both 1Ce10ScSZ and 1Hf10ScSZ were white in colour, and they remain white after ageing in air for 3000 h. Similar is the case with 1Hf10ScSZ sample aged in reducing conditions at 600 °C. However, the colour of the 1Ce10ScSZ sample transforms from white to dark orange on ageing in reducing conditions for 3000 h [12].

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