



# Ionic conductivity ageing investigation of 1Ce10ScSZ in different partial pressures of oxygen

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## ABSTRACT

The conductivity and its ageing behaviour has been determined for zirconia co-doped with 10 mol% of Sc<sub>2</sub>O<sub>3</sub> and 1 mol% CeO<sub>2</sub> in different partial pressures of oxygen at 600 °C. After 3000 h, samples kept in air, in a humidified mixture of H<sub>2</sub>/N<sub>2</sub> and in humidified H<sub>2</sub> exhibited loss in the ionic conductivity of 9%, 19% and 25%, respectively. The conductivity degradation rates after the first 1000 h were 1.5%/1000 h in air and 4.3%/1000 h in humidified H<sub>2</sub>. For all atmospheres, after 3000 h at 600 °C the conductivity value remained above 10 mS/cm, the minimum value required for viable solid oxide fuel cells. On ageing in reducing conditions, the colour on the surface of the sample changed from white to dark orange, indicating the reduction of Ce<sup>4+</sup> cations, which also explains the higher degradation rate in reducing conditions, than in air. The colour gradient within the sample indicates the progress of the reduction front. The core/shell model was applied on the aged reduced sample, and the conductivity of the reduced region is estimated to be 27% lower than the unaged sample. The conductivity behaviour upon re-oxidation is also investigated in air at 600 °C. The conductivity recovers significantly in the first 500 h, thereafter increasing linearly with time. After 2000 h of re-oxidation in air, the gain in conductivity is 3.7% compared to the as-aged sample.

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## 1. Introduction

For a viable solid oxide fuel cell (SOFC), the electrolyte must have a minimum oxide ion conductivity of 10 mS cm<sup>-1</sup> at the operating temperature [1]. Scandia stabilized zirconia (ScSZ), for example 11 mol% Sc<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> (11ScSZ) fulfils the requirement at 600 °C [2]. At 850 °C, this system has an oxide ion conductivity roughly 1.5 times higher than yttria stabilized zirconia, the preferred electrolyte material for SOFCs operating at 700 °C and above [3]. However, below 600 °C, the highly conductive cubic(c)- phase in 11ScSZ undergoes a phase transition to the rhombohedral β-phase with an abrupt decrease in the conductivity [2,4]. The appearance of the low temperature poor conducting β-phase has been described on the basis of oxygen vacancy ordering [5]. The ordering also occurs over time at higher temperatures resulting in a phase transition from c- to ambient phase, which degrades the ionic conductivity [6]. Previously, attempts were made to stabilize the c-phase to room temperature by substituting 1 mol% of Sc<sub>2</sub>O<sub>3</sub> for other oxides such as Gd<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, and CeO<sub>2</sub> [7–10]. Among various co-doped compositions reported in the literature, ZrO<sub>2</sub> co-doped with 1 mol% CeO<sub>2</sub> and 10 mol% Sc<sub>2</sub>O<sub>3</sub> (1Ce10ScSZ) exhibits the highest ionic conductivity

(~16.7 mS cm<sup>-1</sup>) at 600 °C [10]. Further, it has been reported that co-doping with CeO<sub>2</sub> and Sc<sub>2</sub>O<sub>3</sub> can stabilize the c-phase at temperatures down to ambient [5,10]. In addition to the conductivity requirement mentioned above, the electrolyte should exhibit minimal conductivity degradation over time [1]. Lee et al. [10] tested the long-term stability of 1Ce10ScSZ at 800 °C for 600 h in air. The stable conductivity obtained indicates no phase transition, or other effects such as grain boundary segregation and defect ordering with time. However, the tendency of Ce<sup>4+</sup> to be reduced in the low partial pressures of oxygen (PO<sub>2</sub>) may affect the long-term conductivity of 1Ce10ScSZ. The present work explores this issue by studying the conductivity ageing of 1Ce10ScSZ in different atmospheres at 600 °C. The samples described in this work were synthesized at Universitat Jaume I, Castellón, Spain. The electrical and structural studies were performed at Risø DTU, Denmark.

## 2. Experimental

Polycrystalline samples of 1Ce10ScSZ were synthesized using the commercial powder supplied by Daiichi Kigenso Kagaku Kogyo (DKKK) of Japan. The specific surface area of the powder was 11 m<sup>2</sup> g<sup>-1</sup>, while the density of the powder measured by the Helium Pycnometer was 5.64 g cm<sup>-3</sup>. The starting powder was mixed with a binder and acetone in a planetary ball mill for 24 h, and the slurry was then dried using infrared lamps. The powder was de-agglomerated, and

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subsequently uniaxially pressed into cylindrical pellets ( $\varnothing = 8$  mm) using the pressure of 80 MPa. The green pellets were finally sintered at 1500 °C for 6 h using the heating and cooling rates of 2 °C min<sup>-1</sup> and 5 °C min<sup>-1</sup>, respectively. The relative geometrical density of the sintered samples was calculated to be over 98% of the theoretical density.

The conductivity ageing studies were performed on the sintered samples of 1Ce10ScSZ at 600 °C in different atmospheres. Samples were kept in air, in a gas mixture of 9% H<sub>2</sub>, 1% H<sub>2</sub>O and 90% N<sub>2</sub>, and in a mixture of 99% H<sub>2</sub> and 1% H<sub>2</sub>O (all compositions given by volume). The flow rate of the gases was maintained at 120–130 cm<sup>3</sup> min<sup>-1</sup>. The PO<sub>2</sub> was determined using a Nernst sensor. In the H<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub>O(1%), this was found to be  $5.07 \times 10^{-26}$  atmospheres, while in the H<sub>2</sub>/H<sub>2</sub>O(1%), it was  $1.16 \times 10^{-28}$  atmospheres. For the impedance measurement, Pt paste was brushed onto the pellet to serve as the electrode, and fired at 1200 °C for 1 h. The impedance measurements were performed using a Hioki 3532-50 component analyser over the frequency range of 100 Hz to 1 MHz with the applied amplitude of 100 mV, at regular intervals for a period of 3000 h. Due to the high relaxation frequencies at 600 °C, the grain boundary contributions of the impedance spectrum could not be resolved with confidence. Therefore, it was only possible to determine the total resistance of the sample by fitting the low-frequency part of the spectrum to the circuit L(R<sub>1</sub>Q<sub>1</sub>)(R<sub>2</sub>Q<sub>2</sub>) where R<sub>1</sub> and R<sub>2</sub> are the resistance of the electrolyte and electrode, respectively. The conductivity behaviour was also studied upon re-oxidation of the sample aged in H<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub>O(1%) conditions. The aged sample was kept in air at 600 °C for 2000 h, and impedance measurements were performed in regular intervals.

X-ray diffraction (XRD) patterns were collected with Bruker D8 diffractometer with an incident CuK $\alpha$  radiation. The scanning electron microscopy was performed using Hitachi TM-1000 in a backscattered mode with the accelerating voltage of 15 kV.

### 3. Results and discussion

#### 3.1. XRD

Fig. 1 shows the XRD profiles of an unaged and aged samples collected at room temperature. The unaged sample exhibits predominantly *c*-phase with the slight amount of the  $\beta$ -phase. This shows that for the DKKK powder, the addition of 1 mol% CeO<sub>2</sub> is insufficient to completely stabilize the high-temperature *c*-phase to ambient temperature. The best estimate of the lattice parameter was calculated using the Nelson–Riley extrapolation method [11]. The

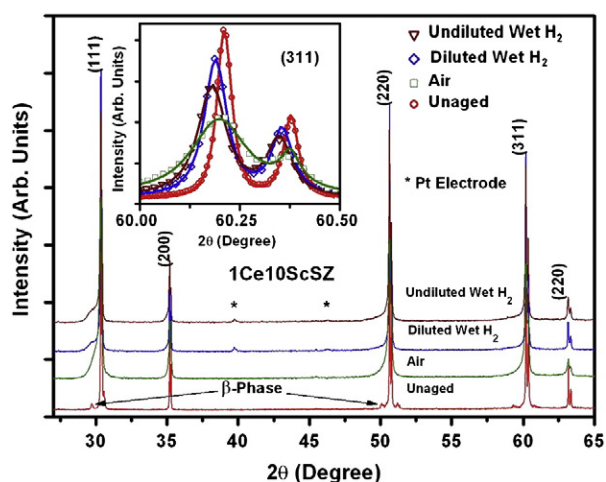


Fig. 1. XRD profiles of the aged and unaged samples of 1Ce10ScSZ. In the inset, (311) peak of all the samples is shown. The dots are the experimental data while the line is the symmetric Pearson VII peak fit.

lattice parameter of the *c*-phase in the unaged sample was estimated to be 5.09281(7) Å. The two extra peaks present in the XRD profiles of the aged samples are due to Pt electrodes. The XRD profiles of all the aged samples show the presence of *c*-phase. Although, the diffraction peaks of  $\beta$ -phase are not distinctly observed in the profiles of the aged samples, a broad peak on the lower  $2\theta$  side of the cubic (111) peak indicates the presence of this phase. Thus, no phase transformation is observed during the ageing process. In the inset of the Fig. 1, (311) peak of all the samples is shown. The peak in the samples aged in reducing conditions shifts toward lower angles, indicating lattice expansion, while the peak shift for the sample aged in air is much smaller. The lattice expansion in the sample aged in reducing conditions can be attributed to the reduction of Ce<sup>4+</sup> cations to Ce<sup>3+</sup> ( $r^{3+}_{\text{Ce,VIII}} = 1.143$  Å,  $r^{4+}_{\text{Ce,VIII}} = 0.0970$  Å) [12]. The lattice parameter of the samples aged in air, in H<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub>O(1%), and in H<sub>2</sub>/H<sub>2</sub>O(1%) was estimated to be 5.0932(2) Å, 5.0941(2) Å and 5.0945(1) Å, respectively.

#### 3.2. Microstructure

Fig. 2 shows the backscattered electron micrograph of the sample aged in H<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub>O(1%). The sample is densely sintered without any isolated residual pores consistent with the high geometrical density and with an average grain size of 6–8  $\mu\text{m}$ . Fig. 2 also shows the optical images of the cross-section of the aged and the re-oxidised samples sectioned along the longitudinal-axis of the cylindrical pellets. The Pt electrodes are on the top and the bottom surfaces of the rectangular cross-section. After ageing in air, no change in the physical appearance of the 1Ce10ScSZ sample was observed. However, the white colour of the unaged sample transforms to dark orange on ageing in reducing conditions. The colour transformation is due to the reduction of 1 mol% Ce<sup>4+</sup> cations homogeneously dissolved in the ZrO<sub>2</sub> lattice. Further, the intensity of the dark orange colour decreases gradually from the surface to the bulk of the sample from all the directions, irrespective of the presence of Pt electrodes. The white colour in the bulk corresponds to the unreduced part of the sample. The presence of the colour gradient suggests the incomplete reduction of Ce<sup>4+</sup> in 1Ce10ScSZ even after ageing for such a long period. Since the reduction does not proceed any faster in the vicinity of the Pt electrodes, we conclude that the reduction process is controlled by the ambipolar diffusion of oxide vacancies and electrons rather than the surface exchange kinetics. The electronic conductivity in doped ZrO<sub>2</sub> is significantly lower than the oxide ion conductivity and, therefore, is rate limiting [13]. Even though the presence of Ce promotes electronic conduction, its concentration is small and the reduction in 1Ce10ScSZ is limited by the diffusion of free electrons in the solid.

The cross-section of the re-oxidised sample aged in H<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub>O(1%) is also shown in Fig. 2. The dark orange colour of the aged sample transforms to cream colour upon re-oxidation in air. The surface and the bulk of the sample appear to be white in colour, while the dark orange colour gradient exists in between. The thin white layer on the surface is due to the incomplete re-oxidation of Ce<sup>3+</sup> cations to Ce<sup>4+</sup>. The slow re-oxidation process can be again explained by the low electronic conductivity of the material.

#### 3.3. Ionic conductivity

The conductivity of the unaged sample of 1Ce10ScSZ was measured as a function of temperature. The activation energy was calculated from the gradient of the quadratic fit of the Arrhenius plot. The total ionic conductivity is determined to be 18.9 mS cm<sup>-1</sup> with the activation energy of 1.023 eV at 600 °C in air. The obtained conductivity value is the highest ever reported for the 10ScSZ co-doped with other cations. Lee et al. [10] measured 16.7 mS cm<sup>-1</sup> for a sample of the same composition, while Wang et al. [14] obtained 13.2 mS cm<sup>-1</sup>, both at 600 °C. The discrepancy in the conductivity

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