



## Ionic conductivity in multiply substituted ceria-based electrolytes

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### ABSTRACT

Cerias, appropriately doped with trivalent rare earth ions, have high oxide ion conductivity and are attractive SOFC (solid oxide fuel cell) electrolytes. Here, seven compositions of  $\text{Ce}_{0.8}\text{Sm}_x\text{Gd}_y\text{Nd}_z\text{O}_{1.9}$  (where  $x$ ,  $y$  and  $z = 0.2, 0.1, 0.0667$  or  $0$  and  $x + y + z = 0.2$ ) are synthesised using a low temperature method in order to determine the effect of multiple doping on microstructure and conductivity. Analysis using scanning and transmission electron microscopy, inductively coupled plasma mass spectrometry, X-ray diffraction and impedance spectroscopy is carried out. Crystallite sizes are determined in the powders and relative densities and grain size distributions were obtained in sintered pellets. Total, bulk and grain boundary conductivities are obtained using impedance spectroscopy and corresponding activation energies and enthalpies of ion migration and defect association are calculated. The highest total conductivity observed at  $600\text{ }^\circ\text{C}$  is  $1.80\text{ Sm}^{-1}$  for  $\text{Ce}_{0.8}\text{Sm}_{0.1}\text{Gd}_{0.1}\text{O}_{1.9}$  and an enhancement effect on conductivity for this combination of co-dopants between  $300\text{ }^\circ\text{C}$  and  $700\text{ }^\circ\text{C}$  relative to the singly doped compounds -  $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$  and  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$  - is seen. This has interesting implications for their application as SOFC electrolytes, especially at intermediate temperatures.

### 1. Introduction

The clean and efficient generation of electricity is a pressing global challenge. Fuel cells convert chemical energy from a gaseous fuel and oxidant directly into electrical work and SOFCs in particular exhibit high efficiencies, low pollutant emissions, fuel flexibility and suitability for Combined Heat and Power applications [1]. Therefore, SOFCs are likely to play an important part in energy conversion in the near future and are being developed for commercial applications ranging from domestic units to small power stations [2,3,4]. So far, widespread use of SOFCs has been inhibited by their high operating temperatures of typically  $800$  to  $1000\text{ }^\circ\text{C}$  [5]. A move to Intermediate temperature (IT)-SOFCs - which operate between  $500$  and  $750\text{ }^\circ\text{C}$  - is desirable in order to widen the range of structural and functional materials that can be used, and reduce energy usage, electrode sintering, interfacial diffusion between electrolyte and electrodes and thermal stress [6,7]. However, the lower ionic conductivity of the electrolyte at these lower temperatures can limit the performance of IT-SOFCs. Therefore, optimising electrolyte design to increase conductivity to acceptable levels at these temperatures becomes central.

Electrolytes based on ceria demonstrate higher oxide ion conductivity at IT than YSZ (yttria-stabilised zirconia), the most commonly used electrolyte in SOFCs. A structure containing a large number of interconnected, equivalent and partially occupied sites for the oxide ion is required for high intrinsic (or ‘bulk’) ionic conductivity. This is

achieved by aliovalent doping of the material - the partial substitution of  $\text{Ce}^{4+}$  ions by tri- or divalent cations in order to create oxygen vacancies to maintain charge neutrality [8]. The relatively facile migration of these vacancies in the cubic anionic sublattice at elevated temperatures then gives rise to fast ionic transport through the electrolyte [9].

Reports have shown that ceria doped with certain trivalent rare earth ions gives higher bulk ionic conductivity than those doped with other elements [10]. The concept of matching the size of the trivalent dopant ion to that of  $\text{Ce}^{4+}$  ( $0.97\text{ \AA}$ ) in order to minimise both strain and activation energy for oxygen vacancy diffusion,  $E_a$ , is an important consideration [11,12,13]. In this approach, to optimise bulk ionic conductivity, the repulsive elastic (related to dopant radius) and attractive electronic components of the interaction between vacancies and dopant ions should balance. According to research by Andersson et al. using *ab initio* methods, this is the case for a hypothetical atomic number between 61 (Pm) and 62 (Sm). Pm is radioactive, so a combination of alternative lanthanide dopant ions with an average atomic number between 61 and 62 was proposed to optimise bulk ionic conductivity in electrolytes based on ceria [14]. This hypothesis was investigated experimentally in work by Omar et al. in which  $\text{Sm}^{3+}$  and  $\text{Nd}^{3+}$  were selected to form electrolytes of composition,  $\text{Sm}_{x/2}\text{Nd}_{x/2}\text{Ce}_{1-x}\text{O}_{2-\delta}$  (with  $x = 0.01$ – $0.2$ ), in which the average atomic number of the dopants was therefore 61. The authors interpreted the adherence of this compositional series to a linear relationship between  $x$  and unit cell

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parameter,  $a$  (Vegard's law) as an indication that less short-range ordering of oxygen vacancies and dopant cations occurred in these materials than in singly-doped materials, such as the series,  $\text{Nd}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ , reported by Stephens and Kilner which displayed a second-order dependence [15]. This lack of defect ordering was proposed to result from a similarity in energy of the sites available to host oxygen ion vacancies which was given in turn as the reason for improved ionic conductivity. At 550 °C,  $\text{Sm}_{0.05}\text{Nd}_{0.05}\text{Ce}_{0.90}\text{O}_{2-\delta}$  was found to have a higher bulk ionic conductivity than the widely used, analogous composition,  $\text{Gd}_{0.10}\text{Ce}_{0.90}\text{O}_{2-\delta}$ , so supporting the hypothesis of Andersson described above [16].

The ideal average atomic number between 61 and 62 also corresponds to a critical dopant ionic radius ( $r_c$ ). Omar et al. ensured that the average dopant ionic radius of the synthesised  $\text{Lu}_x\text{Nd}_y\text{Ce}_{1-x-y}\text{O}_{2-y}$  matched  $r_c$  for all compositions in order to investigate the effect of elastic strain in the lattice on bulk ionic conductivity [17]. It was found that the elastic strain in the doubly doped system was negligible compared to the parent singly doped systems and that the bulk ionic conductivity was higher for the doubly doped system than for the corresponding singly doped systems. Therefore, it was concluded that co-doping based on  $r_c$  can lead to increased conductivity for ceria electrolytes. In a later paper, however, the same authors concluded that  $r_c$  alone was insufficient to fully explain the conductivity of doped cerias [18].

Wang and co-workers observed a higher total conductivity for  $\text{Ce}_{0.85}\text{Gd}_{0.15-y}\text{Sm}_y\text{O}_{1.925}$  ( $0.05 \leq y \leq 0.1$ ) than for  $\text{Ce}_{0.85}\text{Gd}_{0.15}\text{O}_{1.925}$  or  $\text{Ce}_{0.85}\text{Sm}_{0.15}\text{O}_{1.925}$  between 500 and 700 °C [19]. This was attributed to suppression of the ordering of oxygen vacancies and hence to a lower activation energy for the co-doped ceria than for the singly doped ceria. Anirban and co-workers observed that ceria co-doped with  $\text{Gd}^{3+}$  and  $\text{Nd}^{3+}$  exhibited a slight increase in bulk conductivity and a more significant increase in grain boundary conductivity compared to the singly doped specimens with the same dopant concentration with the effect of co-doping increasing at 600 °C and above [20]. Liu and co-workers found that, of all the  $\text{Sm}^{3+}$  and  $\text{Nd}^{3+}$  co-doped and singly doped compositions investigated, the highest total ionic conductivity was observed for  $\text{Ce}_{0.8}\text{Sm}_{0.1}\text{Nd}_{0.1}\text{O}_{1.9}$  [21]. These studies show that co-doping can have beneficial effects on the conductivity of ceria-based electrolytes. However, computational work by Burbano and co-workers predicted that the bulk ionic conductivity of co-doped systems lies within the range spanned by the singly doped materials between 600 and 1000 °C [22]. Whether the co-doping of ceria has a synergistic, detrimental or averaging effect on ionic conductivity will determine which compositions emerge as the most promising ceria-based electrolytes and whether these can be successfully applied in IT-SOFCs.

There is no overall consensus on the best dopant or combination of dopants for ceria-based electrolytes. Therefore, in this work, seven nanopowders with the composition  $\text{Ce}_{0.8}\text{Sm}_x\text{Gd}_y\text{Nd}_z\text{O}_{1.9}$  where  $x$ ,  $y$  and  $z = 0.2, 0.1, 0.667$  or  $0$  and  $x + y + z = 0.2$  were synthesised. The chemical composition, powder nanostructure and crystal phase of these products were studied as were the microstructure and total, bulk and grain boundary ionic conductivities of the dense electrolyte pellets prepared from these powders. The results and analyses were cross-compared to gain insight into the parameters determining favourable performance in these materials.

## 2. Experimental

Seven compositions of  $\text{Ce}_{0.8}\text{Sm}_x\text{Gd}_y\text{Nd}_z\text{O}_{1.9}$  were prepared where  $x$ ,  $y$  and  $z = 0.2, 0.1, 0.667$  or  $0$  and  $x + y + z = 0.2$  (see Table 1).  $0.1 \text{ mol dm}^{-3}$  solutions were made by dissolving stoichiometric amounts of metal nitrate hexahydrates,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Acros Organics, 99.5%),  $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Acros Organics, 99.9%),  $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Acros Organics, 99.9%) and  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Aldrich, 99.9%) separately in deionised water. They were stirred for 3 h to homogenise before being combined. A  $0.2 \text{ mol dm}^{-3}$  citric acid solution was made by dissolving anhydrous citric acid (Alfa Aesar, 99.5%)

in deionised water and stirring for 3 h to homogenise prior to being added to the metal cation solution in the ratio of 1 mol of total metal cations to 2 mol of citrate. The resulting solution was stirred for 12 h to achieve homogenisation, heated to 80 °C and maintained under stirring for 24 h. Evolution of steam and gas resulted in a gel and finally a solid yellow foam. Thermal decomposition of the foam was carried out in a muffle furnace at 250 °C for 2 h and the resulting powder was calcined in a muffle furnace at 500 °C for 2 h. Heating and cooling rates were  $2.5 \text{ °C min}^{-1}$  and  $5 \text{ °C min}^{-1}$  respectively. The powders were dry ground for 1 h at 400 rpm in a planetary ball mill (Fritsch Pulverisette 7) [23] using Nylon jars and 10 mm diameter zirconia balls as the grinding medium and a powder to ball weight ratio of 1:10. It was necessary to suspend the ball milling process every 15 min in order to displace the powder from the walls of the jar. The seven resulting nanopowder compositions underwent detailed characterization.

To make sintered electrolyte pellets, the powders were uniaxially pressed at 200 MPa in a 25 mm (for impedance spectroscopy) or 10 mm (for examination using SEM, scanning electron microscopy) diameter, cylindrical stainless steel die. The pellets were sintered at 1450 °C for 4 h with a heating rate of  $2 \text{ °C min}^{-1}$  and a cooling rate of  $4 \text{ °C min}^{-1}$  in accordance with the method used previously for the synthesis of samarium doped ceria (SDC) [24]. The sintered pellets were polished using 600 and 1200 grade silicon carbide paper and  $6 \mu\text{m}$  diamond paste (and  $3 \mu\text{m}$  diamond paste for the SEM pellets) resulting in a mirror finish.

XRD (X-ray diffraction) analysis of the samples was carried out using a PANalytical Empyrean diffractometer with  $\text{CuK}\alpha_1$  monochromatic radiation. The external standard used was high-grade silicon powder which allowed correction for instrumental broadening. Data were acquired at room temperature by scanning  $2\theta$  from  $10^\circ$  to  $100^\circ$  with a step size of  $0.017^\circ$  and a step time of 0.95 s. The XRD patterns were fitted using Rietveld operations in the High Score Plus programme.

The nanopowders were dissolved in concentrated nitric acid in Teflon-lined autoclaves at 160 °C for 8 h for analysis by ICP-MS (inductively coupled plasma-mass spectrometry) using an Agilent 7500ce with Ar gas flows of  $0.82 \text{ L min}^{-1}$  (carrier) and  $0.2 \text{ L min}^{-1}$  (makeup). Sample solutions were taken into the nebuliser at a rate of approximately  $1.0 \text{ mL min}^{-1}$ . Three runs for each sample were carried out and each mass was analysed in fully quantitative mode (three points per unit mass).  $^{140}\text{Ce}$ ,  $^{157}\text{Gd}$ ,  $^{146}\text{Nd}$  and  $^{147}\text{Sm}$  were analysed in no gas mode. Calibration standards were prepared using single element  $1000 \text{ mg L}^{-1}$  stock solutions for Ce, Gd, Nd and Sm (Qmx), diluted with 2%  $\text{HNO}_3$  v/v (Aristar grade, Merck).

SEM images of the pellets were obtained using a JEOL JSM-6700F instrument equipped with a field emission gun at 5.0 kV and were used to carry out statistical grain area analyses on each sample where the areas of many grains ( $> 400$ ) were measured using ImageJ software. For SEM, polished pellets were thermally etched at 1400 °C, employing a dwell time of 1 min. and identical ramp rates to those used in the sintering process. Samples were gold-coated to reduce charging. A JEOL JEM-2011 instrument was used to acquire TEM (transmission electron microscope) images for crystallite size analysis. Samples were prepared by submerging 3 mm holey carbon Cu grids in an ultrasonicated dispersion of the powder in acetone. The Cu grids were dried overnight.

The dimensions and masses of the sintered pellets were used to calculate their densities. Relative density values were obtained by dividing these density values by the corresponding theoretical density,  $\rho_{\text{XRD}}$ , calculated using Eq. 1 from the crystallographic information obtained by XRD, where  $M_i$  is the atomic mass of element  $i$ ;  $x$ ,  $y$  and  $z = 0.2, 0.1, 0.667$  or  $0$  (and  $x + y + z = 0.2$ )  $u$  is the atomic mass unit and  $V$  is the unit cell volume.

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