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Higher conductivity Sm^{3+} and Nd^{3+} co-doped ceria-based electrolyte materials

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Abstract

A co-doping strategy is used to enhance the ionic conductivity of doped ceria. Recent density functional theory has suggested that Pm with atomic number 61, is the ideal dopant exhibiting low activation energy for oxygen diffusion, and consequently high ionic conductivity. Taking the atomic number of Pm^{3+} into account, Sm^{3+} and Nd^{3+} are selected as co-dopants for ceria to test this hypothesis. Different compositions of $Sm_{x/2}Nd_{x/2}Ce_{1-x}O_{2-\delta}(x=0.01–0.20)$ are synthesized using conventional solid state route. The lattice parameters are estimated after the detailed analysis of X-ray diffraction data using least-squares extrapolation technique. The lattice parameter in $Sm_{x/2}Nd_{x/2}Ce_{1-x}O_{2-\delta}$ system obeys Vegard's law, even at higher dopant concentration, indicating that short-range oxygen vacancy ordering is comparatively lower than in other systems. The ionic conductivity of the samples is measured in the temperature range of 250 °C to 700 °C, using two-probe electrochemical impedance spectroscopy technique. The grain contribution to the ionic conductivity for $Sm_{x/2}Nd_{x/2}Ce_{1-x}O_{2-\delta}$ is disc ussed in detail. The grain ionic conductivity of $Sm_{0.075}Nd_{0.075}Ce_{0.85}O_{2-\delta}$ is found to be 30% higher than that of $Gd_{0.10}Ce_{0.90}O_{2-\delta}$ at 550 °C. It is shown that $Sm_{x/2}Nd_{x/2}Ce_{1-x}O_{2-\delta}$ is an electrolyte that obeys the Meyer–Neldel rule. In the high temperature (>475 °C) region, the activation energy shows a minima at 5mol% dopant concentration with the value of 0.62 eV.
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Keywords: Ionic conductivity; Solid oxide electrolyte; Defect interactions

1. Introduction

Solid oxide fuel cell (SOFC) technology promises high efficiency in generating electricity from hydrocarbons. SOFCs based on an yttria stabilized zirconia (YSZ) electrolyte operate at temperature above 700 °C to avoid unacceptably high ohmic losses. High temperatures demand (a) specialized (expensive) materials for the fuel cell interconnect and insulation, (b) time to heat up to the operating temperature, and (c) energy input to arrive at the operating temperature [1]. Thus, a fuel cell design that gives a reasonable power output at intermediate temperatures (400–700 °C) is highly desirable. In recent years, doped ceria electrolytes have opened up the possibility for such intermediate temperatures SOFCs due to their higher ionic conductivity and good thermodynamic stability. Among doped ceria electrolytes, $Gd_{0.10}Ce_{0.90}O_{2-\delta}$ (GDC) is widely accepted as having the highest ionic conductivity [2]. In search of advanced materials, we have investigated co-doping ceria with the main focus of designing an electrolyte that exhibits higher ionic conductivity than that of GDC.

In order to develop electrolytes that show improved ionic conductivity among doped ceria electrolytes, it is imperative to understand the oxygen ions diffusion mechanism and the energy involved during this process. The ionic conductivity (σ) in these oxides can be seen as a thermally activated process. Its dependence on temperature can be expressed by the following empirical relationship:

$$\sigma T = \sigma_o \exp\left(-\frac{\Delta H}{kT}\right) \qquad (1)$$

where T is the absolute temperature, σ_o is the pre-exponential factor, ΔH is the activation enthalpy, and k is the Boltzmann's constant. Keeping the T constant, it is evident from the Arrhenius relationship that a material with maximum σ_o and the minimum ΔH will show higher ionic conductivity. Previous

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work has shown that co-doping results in enhanced ionic conductivity [1,3,4]. This can be attributed to the increase in configurational entropy which consequently enhances σ_o. We applied this approach and used co-dopants to suppress the oxygen vacancy ordering with an aim to enhance the ionic conductivity.

It is well known that the ionic conductivity in doped ceria 61 systems possesses a maximum at a certain dopant concentration. This is typically associated with the electrostatic and elastic interactions between the dopant cation and oxygen vacancy. These interactions result in the short-range oxygen vacancy ordering which consequently forms stable local defect structures or complex defect associates such as $(D_A^{/}–V_{\ddot{O}}–D_A^{/})$ and $(D_A^{/}–V_{\ddot{O}})^{\cdot}$. At lower intermediate temperatures, most of the oxygen vacancies are bound at various traps. Thus, in this temperature regime, ΔH of oxygen diffusion can be seen as a sum of migration enthalpy ($\Delta H_{migration}$) for oxygen ions and the association enthalpy ($\Delta H_{association}$) of the complex defect associates. In order to enhance ionic conductivity, the binding energy associated with complex defect associates should be minimized. This, will in turn, maximize mobile oxygen vacancies. Numerous studies have been performed focusing on understanding the interactions between the dopant cations and oxygen vacancies and minimizing the activation energy for oxygen diffusion [5]. According to Kilner, association energy is minimal when there is no elastic strain present in the host lattice [6]. Using regression analysis, Kim proposed the critical dopant ionic radius (r_c), which is defined as the ionic radius of an ideal dopant that causes neither expansion nor contraction in the host ceria lattice [7]. The high ionic conductivity of $Gd_xCe_{1-x}O_{2-\delta}$ was explained as the ionic radius of Gd^{3+} lies very close to the r_c value. In our previous work, we adopted a Lu–Nd co-dopant strategy based on r_c to minimize the elastic strain in host ceria lattice. Although no lattice strain was detected, the reported ionic conductivity of the Lu–Nd co-doped ceria electrolyte was lower than that of GDC [1].

Recent density function theory work by Andersson et al. has shown that total interaction energy values for the oxygen vacancy sitting in the first nearest neighbor (NN) site and the next to nearest neighbor (NNN) site for Pm^{3+} dopant are almost same [8]. The total interaction energy was calculated taking both elastic and electronic oxygen vacancy–dopant cation interactions into account. Based on the total interaction energy values determined between the oxygen vacancy and different dopant ions, it was suggested that for Pm^{3+}, and for ions to the right of Pm^{3+} in the lanthanide series, oxygen vacancy interacts strongly with the dopant cation when it occupies NN position of the dopant cation. Moreover, cations with atomic number less than the Pm^{3+} in the lanthanide series usually hold oxygen vacancies in the NNN position of the dopant cation. Thus, around Pm^{3+} there will be no site preference for oxygen vacancies, resulting in an increase in the number of equi-interaction energy sites which facilitate the oxygen vacancy diffusion. It was then predicted that Pm^{3+} doped ceria should exhibits higher ionic conductivity than any other singly doped ceria material. Unfortunately, Pm is radioactive and cannot be used for electrolyte applications. The ideal dopant should have an effective atomic number around Pm^{3+} (61) which shows ionic radius of 1.093 Å [9]. Therefore, as proposed by Andersson et al., a co-dopant scheme using Sm^{3+} and Nd^{3+} can provide an experimental scenario for testing this hypothesis. In terms of ionic radii, 1:1 Sm:Nd co-doping can be seen as having an weighed average dopant ionic radius of 1.094 Å (which is close to Pm^{3+} ionic radius of 1.093 Å) [9].

Based on this, in the present work the effect of co-dopant pair Sm^{3+} and Nd^{3+} on the ionic conductivity of ceria-based electrolyte is investigated. Dopants were added in equal proportion to achieve the effective atomic number of Pm^{3+}, i.e. 61. By doing so, similar total interactions between the oxygen vacancies sitting in NN and NNN sites and the dopant cation are expected, with the consequent enhancement of the ionic conductivity.

2. Experimental

Polycrystalline samples of $Sm_{x/2}Nd_{x/2}Ce_{1-x}O_{2-\delta}$ (where $x=0.01$, 0.03, 0.05, 0.08, 0.10, 0.12, 0.15, 0.18, and 0.20) were synthesized by conventional solid state reaction method, starting from stoichiometric mixtures of Sm_2O_3, Nd_2O_3, and CeO_2 powders (all with 99.99% purity). For comparison, phase pure samples of $Gd_{0.10}Ce_{0.90}O_{2-\delta}$ were also processed using identical experimental procedure. The weighed powders were mixed by ball-milling in de-ionized water with 1% dispersant for 24 h, and subsequently dried in the oven at 120 °C for 16 h. The dried ball milled powders were then calcined at 1450 °C for 10 h. To confirm the complete dissolution of dopants in ceria, phase analysis was performed using X-ray diffraction (XRD). Curved position-sensitive diffractometer (INEL, France) was used to obtain the XRD pattern of each composition using Cu K_α radiation. Peak position in the XRD pattern was determined by fitting each individual peak with two symmetric Pearson VII profiles to model both the Cu $K_{\alpha1}$ and Cu $K_{\alpha2}$ components of the incident X-ray beam using a commercially available software. The best estimate of the lattice constant (a_o) for all the compositions of $Sm_{x/2}Nd_{x/2}Ce_{1-x}O_{2-\delta}$ was calculated using the least-squares extrapolation method [10].

After the calcination, agglomerated powders were again ball milled in de-ionized water with 1% dispersant for 24 h followed by drying in the oven at 120 °C for 16 h. The dried calcined powders were then sieved using a 212 µm mesh. Powders were then uniaxially pressed into disk-shaped pellets (8 mm in diameter and 4 mm thick) using polyvinyl alcohol (~1wt.%) as a binder under a pressure of 180 MPa. This was followed by the isostatic pressing at 200 MPa for 3 min. The green ceramic pellets were finally sintered in air at 1550 °C for 10 h. Densities of all the sintered samples were measured in water using Archimedes's principle and were estimated to be 98% of theoretical density or above. The microstructure of the sintered pellets was studied using scanning electron microscope (SEM). The SEM investigations were carried out on polished and thermally etched surfaces.

The as-sintered pellets were then polished to obtain planar surfaces. Pt paste (CL11-5349, Heraeus) was brushed onto both sides of the disk-shaped pellets to serve as the electrode. The pellets were then co-fired at 900 °C for 1 h. Pt wires (99.9% pure)