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Structural and Electrical Properties of Multivalent Pr Doped Ceria: A Short Review

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Abstract

Multivalent Pr doped ceria is a potential candidate for SOFCs due to its mixed electronic and ionic conductivity. The valence state of Pr significantly affects the lattice parameter of Pr doped ceria. The lattice parameter mainly depends on the dopant concentration, sintering and switching of valence state. The concentration oxygen vacancies are responsible for ionic conductivity and the oxidation of Pr^{3+} to Pr^{4+} is the origin of electronic conductivity. The electronic conductivity increases with the doping concentration and the oxygen partial pressure.

Keywords: Pr doped ceria; Mixed conductivity; Oxygen partial pressure

Introduction

Cubic fluorite structured ceria doped with lower valent cations forms exceedingly oxygen vacancies in the doped ceria lattice. Therefore rare earth doped ceria exhibits high oxygen conductivity at elevated temperatures, which makes it potential candidate for solid electrolyte in intermediate temperature solid oxide fuel cells (IT-SOFCs) [1]. Among the different rare earth elements, multivalent Pr draws more attraction due to its ease of Pr^{3+}/Pr^{4+} switching, similar structure to that of ceria and ionic radius closed to Ce^{4+} ions, which make Pr doped ceria as oxygen storage materials and oxygen ion conducting solid electrolytes [2,3]. Again, Pr doped ceria exhibits pink-orange to red-brown colored nano-particles depending on the synthesis process, sintering temperature, dopant concentration, etc. [4]. Takasu et al. [5] reported that multivalent Pr doped ceria can be used as an oxide electrode due to its high electronic and ionic conductivity. Again Ahnet al. [6] reported that Pr^{3+} have been included as preponderance ions in Pr-doped ceria which indicates higher ionic conductivity than electronic conductivity in Pr doped ceria. However, electronic conductivity is due to small polar on hoping of electrons between Pr^{3+} and Pr^{4+} ions and the ionic conductivity is due to the formation of oxygen vacancies [7]. In this mini review, structure and mixed conductivity of Pr doped ceria have been discussed.

Discussion

The single phase cubic fluorite structure with space group Fm3m of Pr doped ceria has been confirmed from the XRD patterns by the several researchers [4,8-10]. de Larramendi IR, et al. [10] reported that the lattice parameters of Pr doped ceria as 5.4117(4), 5.4097(9) and 5.4234 (1) Å for the samples prepared by ceramic, sol-gel and modified polyol routes, respectively. The lattice parameters was found to increase with Pr concentration [4,8] which is due to the higher ionic radius of Pr^{3+} (1.126 Å) than Ce^{4+} (0.97 Å). Since ionic radius of Pr^{4+} (0.94 Å) is slightly lower than Ce^{4+} thus lattice expansion due to Pr doping indicates Pr^{3+} is the major dopant cautions. According to Chiba R, et al. [9] lattice parameter of Pr doped ceria decreases with dopant concentration at lower temperature but increases at higher temperature. Y. Takasu et al [11] also reported decreases in lattice parameter with Pr concentration. The contradiction in results my due to the different synthesis route which is responsible for different Pr^{3+}/Pr^{4+} ratio in the formed ceria based solid solutions. However, the rate of increase of lattice parameter with dopant concentration depends on Pr^{3+}/Pr^{4+} switching with the sintering temperature [8].

The ionic conductivity in Pr doped ceria depends on the formation of free oxygen vacancies due to the substitution of Ce^{4+} ions by Pr^{3+} which is represented by the Kröger-Vink notation as:

$$Pr2O_3 + 2CeO_2 \rightarrow 2PrC_e{}' + 3O_o x + V_o{\bullet\bullet} \qquad (1)$$

Since Pr is multivalent the concentration of free oxygen vacancies may decreases due to the oxidation of Pr^{3+} to Pr^{4+} as represented by

$$2Pr_{Pr} + 3V_{o}{\bullet\bullet} + 1/2O2 \rightarrow Pr_{Pr}^{x} + 3O_{o}x \qquad (2)$$

Therefore with the Pr concentration the ratio of ionic to electronic conductivity decreases in Pr doped ceria. Shunk, et al. [12] reported that the electronic conductivity exceeds the ionic conductivity at doping concentration >25%. It is also reported that at very low dopant concentration (<2%), Pr doped ceria exhibits p-type electronic conduction at 0.2atm or a high oxygen partial pressure but at high doping concentration it exhibits n-type electronic conduction [9]. Anirban SK, et al. [8] has been investigated the sintering effect on Pr doped ceria and was found fall in ionic conductivity at higher sintering temperature due to the oxidation of Pr^{3+} to Pr^{4+} and formation of defect association which is reduces the free oxygen vacancies. The oxygen vacancy and electron concentration in Pr doped ceria is very sensitive to temperatures at which conductivity changes abruptly and this temperature decreases with doping concentration [9]. Using kinetic lattice Monte Carlo model for oxygen vacancy diffusion in Pr doped ceria Dholabhai PP, et al. [13] observed maximum in ionic conductivity at 15-30% dopant concentration. Again the conductivity of multivalent Pr doped ceria strongly depends on the oxygen partial pressure, unlike than other trivalent doped ceria in which the ionic conductivity is independent of oxygen partial pressure. The oxidation of Pr^{3+} to Pr^{4+} increases with oxygen partial pressure and at sufficiently high oxygen partial pressure most of the Pr takes on the +4 state and ionic conductivity exhibits a power law dependence on oxygen partial pressure with a -1/6 slope [14]. The electronic conductivity of Pr doped ceria predominant at higher oxygen partial pressure. Since Pr is mixed valent thus the small polar on hopping of electrons on Pr^{3+} sites can only hope to a neighboring empty Pr site or in the Pr^{4+} state. Thus the electronic conductivity due to small polar on is proportional to the product Pr^{3+} and Pr^{4+}concentration and shows a maximum conductivity as a function of oxygen partial pressure where the concentrations of Pr^{3+} and Pr^{4+} are equal.

Conclusion

The valence state of Pr in Pr doped ceria depends on the synthesis process, sintering temperature and oxygen partial pressure. Depending on the valence state of Pr the lattice parameter of Pr doped ceria may increase or decrease. The oxidation of Pr suppresses the oxygen vacancies and increases the electronic conductivity. The values of mixed electronic-ionic conductivity depend on the dopant concentration and oxygen partial pressure. The maximum conductivity has been obtained at the equal concentration of each valence state of Pr in Pr doped ceria.

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