



Praseodymium doped ceria as electrolyte material for IT-SOFC applications

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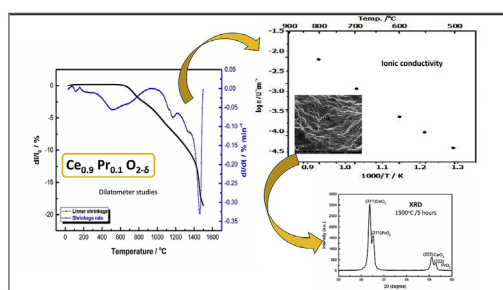
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HIGHLIGHTS

- Praseodymium doped ceria (PDC) electrolyte was synthesised by EDTA citrate method.
- Dilatometer study revealed multiple shrinkage behaviour of PDC.
- PDC showed an ionic conductivity of $1.213\text{E-}03\text{ S cm}^{-1}$ at $700\text{ }^{\circ}\text{C}$.
- XRD at $1500\text{ }^{\circ}\text{C}$ revealed that they crystallize as fluorite CeO_2 + cubic PrO_2 phase.

GRAPHICAL ABSTRACT



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ABSTRACT

Praseodymium-doped ceria (PDC, $\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_2$) electrolyte material for intermediate temperature solid oxide fuel cells (IT-SOFCs) has been successfully synthesised by EDTA-citrate method. From X-Ray diffraction (XRD), fluorite structure along with a crystallite size of 5.4 nm is obtained for PDC nanopowder calcined at $350\text{ }^{\circ}\text{C}/24\text{ h}$. Raman spectroscopy confirmed the structure, presence of oxygen vacancies with the manifestation of the main peak at 457 cm^{-1} and with a secondary peak at 550 cm^{-1} . From Transmission Electron Microscopy (TEM) analysis, the average particle size is around 7–10 nm and selected area electron diffraction (SAED) patterns further confirmed the fluorite structure of PDC nanopowder. The PDC nanopowder displayed a BET surface area of $65\text{ m}^2/\text{g}$ with a primary particle size of $\sim 13\text{ nm}$ (calculated from BET surface area). Dilatometer studies revealed a multi-step shrinkage behaviour with the multiple peaks at 522, 1171 and $1461\text{ }^{\circ}\text{C}$ which may be originated due to the presence of multiple size hard agglomerates. The PDC electrolyte pellet sintered at $1500\text{ }^{\circ}\text{C}$ displayed an ionic conductivity of $1.213\text{E-}03\text{ S cm}^{-1}$ along with an activation energy of 1.28eV. Instead of a single fluorite structure, XRD of sintered PDC pellet showed multiple structures (Fluorite structure (CeO_2) and cubic structure (PrO_2)).

1. Introduction

Solid oxide fuel cells (SOFCs) are considered as a promising device for electrochemically converting a gaseous fuel in to useful energy with

higher conversion efficiency and less environmental impact [1]. One of the main components of SOFC systems include dense solid oxide ion conducting ceramic electrolyte membrane sandwiched between cathode and anode. The well-known oxygen ion conducting ceramic

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electrolyte materials for SOFC includes cubic stabilized zirconia, doped cerium based oxides, bismuth based oxides and lanthanum gallate based oxides. Ytria stabilized zirconia is considered as the most preferred electrolyte material for SOFC at high temperatures because of its high ionic conductivity, high chemical and mechanical stability. But the disadvantage of this system is that higher operating temperature leads to high fabrication cost, mismatch in thermal expansion coefficient and causes reaction between the cell components [2]. Therefore, it becomes necessary to decrease the operating temperature and to develop electrolyte materials in the intermediate temperature range to commercialize the technology. Problems of lanthanum gallate oxide based electrolyte system sintered at higher temperature includes the volatilization of gallium(I) oxide (Ga_2O) from the perovskite structure and thereby reduces the overall ionic conductivity of the electrolyte material [3]. In spite of remarkably high ionic conductivity, bismuth oxide based electrolytes possess drawbacks such as thermodynamic, structural and chemical instability and pure bismuth oxide undergoes phase transformations from cubic to monoclinic on cooling below 730°C resulting in a drop in ionic conductivity [4,5]. Among all these materials, rare-earth doped ceria has been found to be a promising electrolyte for IT-SOFCs operating at temperature lower than 700°C [2,6–10].

Ceria based materials have found applications in various fields apart from SOFCs, such as oxygen sensors [11], catalyst/photo catalyst [12], UV blockers [13] and oxygen storage capacitors [13]. Apart from this, photo catalytic degradation of organic dyes using cerium oxide catalyst in UV/visible beams are considered as an effective way in removing the organic contaminants due to biodegradable nature of pollutants is yet another application of cerium oxide [14]. Since nano particles exhibit promising properties that are different from their relative bulk properties, cerium oxide nanoparticles has been widely used in many above mentioned applications mainly due to the low energy band gap between Ce^{3+} and Ce^{4+} , high mobility and also due to high oxygen storage capacity.

Rare earth doped ceria based materials possess lower activation energy and high ionic conductivity at relatively lower temperature as compared to YSZ electrolyte and show good promise in replacing state-of-the-art YSZ as the electrolyte materials. At 1000°C , YSZ exhibit an ionic conductivity higher than 0.1 S cm^{-1} ; coefficients of thermal expansion similar to the other cell components, high ionic conductivities ($> 0.1\text{ S cm}^{-1}$) at intermediate temperatures, and chemical stability during cell operations are the important aspects to be considered for a ceramic material to be used as an electrolyte material [15]. Moreover, at lower temperatures the cell performance is decreased in case of YSZ material. Thus, ceria based ceramics are considered as the most promising electrolyte material for SOFC because of its high ionic conductivity which in turn reduces the operating temperature and eliminates the technical issues. The enhancement of ionic conductivity in doped ceria is mainly due to oxygen ion vacancies [6].

Some of the reports on Praseodymium-doped ceria materials (PDC) indicate that it can be a candidate for electrolyte materials for SOFCs [16,17]. Pr cation can exist in two oxidation states ($\text{Pr}^{3+}/\text{Pr}^{4+}$) and promote oxygen vacancies, and its presence in ceria lattice alters the grain boundary behaviour of the oxide system and thus enhances the conductivity [18,19]. For Pr doped ceria, the density of the anion vacancies is lower when compared to the other dopants like gadolinium and samarium, and this can be due to the presence of multi valance state [20]. A massive increase in chemical expansion upon heating is another critical anomalous behaviour of PDC [21], which can cause stoichiometric or phase change expansion. Above-mentioned desirable properties motivated the present study to explore/synthesise PDC nanopowder as an alternative electrolyte material for IT-SOFCs.

According to literature, PDC has been synthesised by variety of techniques such as hydrothermal method [22], sol gel method [23], flux method [24], co-precipitation method [25], combustion synthesis [17] etc. When compared to various synthesis methods, EDTA-citrate method is used to prepare a wide variety of oxide materials [26,27].

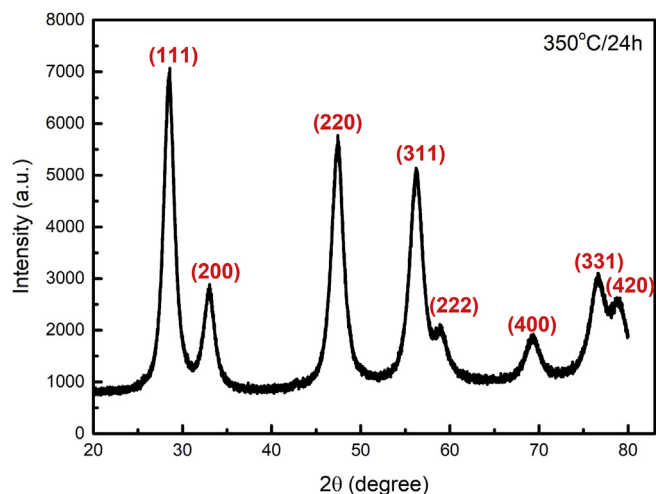


Fig. 1. XRD pattern of PDC sample calcined at $350^\circ\text{C}/24\text{ h}$.

EDTA and citric acid are used as chelating agents, which forms stable complexes. EDTA citrate method offers the possibility for the synthesis of nano scaled particle size with good compositional homogeneity [28].

Nauer et al. [29] reported that cerium-praseodymium oxide forms fluorite-type solid solutions for all samples up to 30 mol% PrO_{2-x} while M. J. Chen et al. [30] obtained single phase fluorite solid solution up to 35 mol%. Wang et al. [16] noticed a decrease in cell parameter for 20-mol% Pr and indicated that the solubility limit for PDC might be around 20 mol%. These differences in regarding the solubility of Pr in CeO_2 may be due to differences in synthesis and processing procedures including the heat-treatment conditions [31]. According to literature several theoretical and experimental studies have suggested 10 mol% of gadolinium oxide and 10 mol% samarium oxide is the best dopant concentration for cerium dioxide to obtain high ionic conductivities [6,32–35]. In the present study, for Pr, a fixed amount of 10 mol% is taken and is synthesised by the EDTA-Citrate complexing method; and physical characterization along with dilatometer study and ionic conductivity measurements were carried out.

2. Experimental

2.1. Powder synthesis

AR grade chemicals Cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, SRL Chemicals $\geq 99\%$), Praseodymium nitrate hexahydrate ($\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Sigma Aldrich Chemicals 99%), EDTA (ethylenediaminetetraacetic acid, Sigma Aldrich Chemicals $\geq 99\%$) and citric acid (Sigma Aldrich Chemicals $\geq 99\%$), Ammonium hydroxide (NH_4OH , 25% ammonia Spectrum reagents) were used for the synthesis of PDC nano-crystalline material by EDTA citrate complexing method. Stoichiometric amounts of Cerium nitrate hexahydrate and Praseodymium nitrate hexahydrate were dissolved in deionised water and the solution is stirred continuously at room temperature. EDTA and citric acid were used as chelating agents. The required amount of EDTA dissolved in NH_4OH for the complete dissolution was then added to the aqueous solution of metal nitrate. Stoichiometric amount of citric acid was added to the resulting solution under continuous stirring to allow citric acid to dissolve completely to obtain a clear solution. Then necessary amount of NH_4OH solution was added to the clear solution to maintain the pH (~ 9) to the desired value. The mole ratio of total metal ions to EDTA and to citric acid used was 1:1:1.5. After homogenisation of the solution, the resulting final solution was heated at 100°C to remove excess water and nitrate gases under continuous stirring condition to obtain a thick, viscous gel. The gel obtained is kept in the hot air oven for 24 h at 150°C temperature in order to convert it to a black

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