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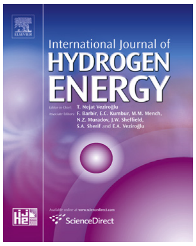

Structural, chemical, and electrochemical properties of co-doped fluorite oxides $Ce_{0.8}La_{0.2-x}Tl_xO_{2-\delta}$ as electrolyte materials for solid oxide fuel cells

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ABSTRACT

A series of fluorite samples with the $Ce_{0.8}La_{0.2-x}Tl_xO_{2-\delta}$ (T_xLDC, x = 0–0.09) composition were prepared via a simple polyol process. Samples were characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM) attached with an energy dispersive X-ray spectroscopy (EDXS) system, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Pycnometer and impedance spectroscopy. Dense ceramics were prepared by sintering the pellets at 1400 °C for 7 h. The results show that the Tl content (x) affects the properties of $Ce_{0.8}La_{0.2-x}Tl_xO_{2-\delta}$. The fluorite with x = 0.07 is suggested as the most promising composition for a solid oxide fuel cell electrolyte material since it has shown to have a high electrical conductivity (3×10^{-2} Scm^{-1} at 650 °C) and a low activation energy (0.69 eV). The ionic conductivity is almost stable at functional temperature (550 °C) for an extended period of time. It is therefore concluded that co-doping with the appropriate amount of Tl has a great potential to become a new important electrolyte for commercial IT-SOFCs.

Introduction

As one of the most promising energy conversion devices, solid oxide fuel cells (SOFC) have the potential to play a key role in the energy conversion landscape in the medium and long term [1–4] because of their high efficiency (up to 85%), low-polluting emissions and fuel flexibility [5,6]. The widespread use of conventional SOFCs has been held back by their high operating temperature (800–1000 °C). Such high temperatures lead to notable problems such as the thermal expansion between cell

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components (electrolyte – electrodes), and the high degradation rate between them due to a lack of flexibility in the selection of materials and the high costs of said materials. To overcome these problems, considerable research efforts have been devoted to lowering their operating regime to something between 400 °C and 700 °C, known as the intermediate temperature (IT) range [7–10]. Nevertheless, one of the challenges for IT-SOFCs is the development of low-cost electrolyte materials with a high durability. An ideal electrolyte material for IT-SOFCs should have high oxide ion conductivity, negligible electronic conduction and be thermodynamically stable over a wide range of temperatures and oxygen partial pressure [11–14]. In this regard, ceria doped with divalent or trivalent cations are strong candidates to act as IT-SOFC electrolytes. Among the currently used doped ceria are those with general formula $Ce_{1-x}M_xO_{2-\delta}$ (where M are rare earth and alkaline earth) [15–36]. These materials have remarkable properties in terms of structural, electrochemical and thermal stability. Doping cerium with a cation of a lower valency than Ce^{4+} introduced an oxygen vacancy in the lattice as charge compensating defects and increased the ionic conductivity [12]. However, when exposed to the reducing atmosphere, their conductivity requires co-doping to obtain acceptable performances and to improve their electrical properties. So far, several studies reporting improvements in ionic conductivity of co-doped ceria with rare earth and/or alkaline earth cations have been carried out [37–58]. There are very few studies where ceria is doped and/or co-doped with rare earth and post-transition metals [59–61]. Since $Ce_{0.8}La_{0.2}O_{1.9}$ has been found to have a good conductivity [19], La^{3+} (1.16 Å) and Tl^{3+} (0.98 Å) [62] co-doped ceria are probably good electrolytes. However, there is still aren't enough of research results on these materials.

In order to obtain pure rare earth doped ceria powders and an improved electrical performance, a number of synthesis methods have been proposed such as Hydrothermal synthesis [18–21], the mechanical milling reaction method [38], the citric acid-nitrate combustion method [37,41], the cellulose templating method [39] etc. Besides the above mentioned methods, the simple polyol process was used for obtaining metallic nanoparticles, preparing phosphor materials and synthesizing oxide powders [69,70]. The basis of this method is to make use of ethylene glycol (EG) as a solvent, a reducing agent and a stabilizer. Materials obtained through this process show small particle distribution and homogenous phase composition.

In the current study, with the aim to develop new ceria-based electrolyte materials with improved electrochemical properties, La^{3+} and Tl^{3+} co-doped ceria materials were prepared for the first time, to the best of our knowledge, via a polyol process. We present the effect of co-doping on structure, microstructure and the electrical properties of the abovementioned materials and the comparison of the results of co-doped materials with singly doped ones.

Experimental

Sample preparation

A series of solid solutions of electrolytes with the general formula $Ce_{0.8}La_{0.2-x}Tl_xO_{2-\delta}$ (denoted T_xLDC; x = 0, 0.03, 0.05, 0.07, 0.09) were synthesized by a simple polyol process as reported in the literature [30]. Stoichiometric amounts of Cerium (III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$, 99%, Aldrich), lanthanum (III) nitrate hexahydrate ($La(NO_3)_3 \cdot 6H_2O$, 99%, AppliChem) and thallium (III) nitrate hydrate ($Tl(NO_3)_3.3H_2O$, 99%, Aldrich) were dissolved in 50 ml of ethylene glycol EG ($C_2H_6O_2$, AppliChem) by using a two-necked spherical glass flask equipped with a refluxing condenser and a thermometer, and submerged into a heating oil bath with stirring. The metal precursors were dissolved in the reducing agent and placed under constant stirring at 60 °C/1 h for uniform mixing. The reaction mixture was then heated at 200 °C for 5 h under reflux conditions and vigorous stirring until the precipitation was completed. The reaction was followed through its distinctive color changes from white to light yellow and then to light brown. After 5 h reacting, the solution was cooled to room temperature and the precipitate of the as-synthesized material obtained, was washed (lavage) passed two times by centrifugation in ethanol and distilled water to remove any excess EG. The powders were dried at 70 °C for 10 h in a hot air oven. After being crushed in an agate mortar, the powders were calcined in air at 750 °C for 5 h in order to obtain the desired compound, the purity of which was proved by X-ray characterization.

Structural measurement

The composition phase of the obtained T_xLDC powders was identified by X-ray diffraction (XRD) with a Bruker D8 Advance (Germany) diffractometer which uses Cukα1 monochromatic radiation at room temperature. The crystalline phase and cell parameters were fitted with Rietveld refinements of the XRD patterns using the FULLPROF software. The average crystallite size (D) was also defined by using the Scherrer formula: $0.9\lambda/\beta\cos\theta$. The morphology of the pellets and the microstructure of the T_xLDC powders were observed with a scanning electron microscope (SEM), JEOL.JSM-5400 and by transmission electron microscopy (TEM) using a FEI Tecnai G2 transmission electron microscope operating at 200 kV with an LaB_6 filament. A local chemical analysis was performed using an energy dispersive X-ray spectroscopy (EDXS) system attached to the TEM. The dried powders were ground in an agate mortar and then pressed at 50 MPa into cylindrical pellets (10–12 mm in diameter and 0.6–0.8 mm in thickness). At first, the pellets with formula $Ce_{0.8}La_{0.2}O_{2-\delta}$ (LDC) were sintered at 1200 °C, 1300 °C, 1400 °C and 1500 °C. Then, the $Ce_{0.8}La_{0.2-x}Tl_xO_{2-\delta}$ (T_xLDC) pellets were sintered at 1400 °C. All pellets were sintered in air for 7 h with a heating and cooling rate of 4 °C/min. Experimental densities of the sintered pellets were determined using a Pycnometer with distilled water and were then compared to the theoretical values determined from the lattice parameters. The X-ray photoelectron spectroscopy (XPS) measurement was performed using a conventional Al K (h = 1486.6 eV) photon source (OmicronDAR 400) and a hemispherical electron spectrometer (OmicronEA 125). The base pressure of the analysis chamber was typically $\approx 10^{-10}$ mbar. The sintered $T_{0.07}$LDC sample was repeatedly flashed to 1000 °C for 30 s until any traces of the oxide layer and carbon contaminant were removed. XPS binding energies (BEs) refer to the Fermi level.