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Electrolyte materials for solid oxide fuel cells derived from metal complexes: Gadolinia-doped ceria

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Abstract

Gadolinia doped ceria (GDC) powders with different gadolinium contents were successfully prepared by the thermal decomposition of ceria complexes. All the calcined powder samples were found to be ceria-based solid-solutions having a fluorite-type structure. The powders were cold-isostatically pressed and sintered in air at 1500 °C for 5 h to attain a sintered density of about 90% of its theoretical value. The electrical conductivity of the GDC pellets in air was studied as a function of temperature in the 225–700 °C range, by using two-probe electrochemical impedance spectroscopy measurements. The highest total conductivity ($\sigma_{600\,^{\circ}\mathrm{C}} = 0.025$ S/cm) was found for the $Ce_{0.85}Gd_{0.15}O_{1.925}$ composition.

Keywords: A. Powders: chemical preparation; C. Ionic conductivity; D. CeO_2; E. Fuel cells

1. Introduction

Solid oxide fuel cells (SOFCs) using oxygen-ion conducting electrolytes offer a low-pollution technology to directly convert chemical energy into electricity with high efficiency [1]. The advantages of SOFCs over other conventional energy conversion systems include high efficiency, modularity, fuel adaptability, and very low levels of emissions depending on the fuel used [2]. However, SOFC operation needs elevated temperatures, above 900 °C, due to the use of yttria-stabilized zirconia (YSZ) as the electrolyte material, which results in high costs and in decreasing the durability, due to electrode sintering and interfacial reactions. Improved durability, a wider choice for interconnecting material selection, and lower costs can be achieved by reducing the operating temperature below 700 °C [3].

For this purpose, electrolytes with high oxygen-ion conductivity at low temperatures are under investigation. Moreover, reducing the electrolyte thickness decreases the electrolyte ohmic resistance. Gadolinia-doped ceria (GDC) is an attractive electrolyte alternative to YSZ, owing to its superior oxygen ion conductivity at low temperatures [4,5]. Ceria doping is needed to increase the oxygen vacancy concentration and to reduce the intrinsic electronic conductivity. Among the various doping elements investigated, Gd^{3+} and Sm^{3+} doped ceria (GDC and SDC) were reported to have the largest conductivity [6]. Moreover, studies have been carried out on co-doped ceria [7–10].

Currently, the common synthesis routes to prepare doped ceria powders include solid-state reaction [11,12], co-precipitation reaction [12–15], hydrothermal synthesis [16] and sol–gel routes [17]. However, these synthesis routes have some

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disadvantages, such as the cost of the starting materials, complexity, slowness, lack of homogeneity and purity, and high processing temperature. SOFC electrolyte materials usually possess complex compositions with several metallic elements, and therefore selecting a simple and low-cost method to effectively prepare doped ceria powders has distinct advantages for SOFC research.

In a previous work, Laobuthee et al. used a simple and straightforward method to directly prepare Mg–Al–TEA complex from $Al(OH)_3$, MgO and triethanolamine (TEA), as a precursor for magnesium aluminate spinel ($MgAl_2O_4$) via the oxide one pot synthesis (OOPS) process [18]. The obtained $MgAl_2O_4$, exhibiting high purity and homogeneity, was tested as a humidity sensor material [18]. However, this method showed some disadvantages, such as the limited solubility of the starting materials, the high boiling point of the ethylene glycol solvent, and the required reaction temperature at 200 °C. To address these limitations, based on the OOPS process, the nitrate salts were alternatively used as starting materials. Lower boiling point solvents, such as propan-1-ol and butan-1-ol, were also used to replace ethylene glycol. The complexes prepared by modified method were used as precursors for the production of high quality GDC powders, which were sintered into pellets and then characterized their electrochemical properties.

2. Experimental

The starting materials were cerium(III) nitrate hexahydrate [$Ce(NO_3)_3 \cdot 6H_2O$, 99.5% purity] and gadolinium(III) nitrate pentahydrate [$Gd(NO_3)_3 \cdot 5H_2O$, 99.9% purity], purchased from Acros Organics. Triethanolamine [TEA, $N(CH_2CH_2OH)_3$, 98% purity] and propan-1-ol [$CH_3CH_2CH_2OH$, 99.5% purity] were obtained from Carlo Erba (Barcelona). All chemicals were used as provided.

The complexes were prepared by mixing in 80 mL propan-1-ol, $Ce(NO_3)_3 \cdot 6H_2O$ and $Gd(NO_3)_3 \cdot 5H_2O$, with the molar ratios of Ce:Gd = 0.9:0.1, 0.85:0.15, and 0.8:0.2, denoted $Ce_{0.9}Gd_{0.1}O_{1.95}$, $Ce_{0.85}Gd_{0.15}O_{1.925}$, and $Ce_{0.8}Gd_{0.2}O_{1.9}$, respectively. TEA was added in the 1:1 molar ratio of metal ions to TEA. After amalgamation, the as-prepared transparent solutions were distilled for 3 h in order to obtain the complex precipitates. The precipitates were collected by filtration and then washed with propan-1-ol. Simultaneous thermogravimetric and differential thermal analysis (TG/DTA) of the complexes was performed using a TGA/SDTA analyzer (Model TGA/SDTA 851e, Mettler Toledo), in flowing air with a heating rate of 5 °C/min, in the 50–1000 °C temperature range.

The complexes were calcined in an alumina crucible at various temperatures: 400, 600, 800, 1000, and 1200 °C for 2 h. Phase identification was performed using X-ray diffraction analysis (XRD; Philips X-Pert-MPD X-ray diffractometer) operating at 40 kV/30 mA, with monochromated Cu Kα radiation. Diffraction patterns were recorded in the range of $2\theta = 20–90°$ by step-scanning, with a step interval of 0.02° and a scanning time of 2 s for each step.

The specific surface area of the powders, S_{BET}, was measured using the Brunauer–Emmett–Teller (BET) nitrogen-gas absorption method. The values were calculated from the nitrogen absorption isotherms at 77 K, using a Micromeritics ASAP 2020 surface analyzer at a value of 0.162 nm^2 for the cross-section of the nitrogen molecule. Samples were degassed at 350 °C under high vacuum conditions for 20 h before measurements. The specific surface area was converted to particle size (D_{BET}) according to Eq. (1), under the approximation that the particles were closed spheres with a smooth surface and of uniform size.

$$D_{BET} = \frac{6 \times 10^3}{d_{th} S_{BET}} \quad (1)$$

Here, d_{th} was the theoretical density of the material (g/cm^3) and D_{BET} was the average particle size (nm). The specific surface area, S_{BET}, was expressed in m^2/g.

Scanning electron micrographs were obtained using a JEOL JSM-6301F scanning electron microscope (SEM) operating at an acceleration voltage of 12 kV, to identify the powder microstructure. Samples were mounted on aluminum stubs using carbon tape and then sputter coated with Au to avoid particle charging.

The obtained powders were uniaxially pressed into green pellets (~30 MPa) in a stainless steel die of 10 mm in diameter, and then isostatically pressed at ~200 MPa. When not specified, the powders used were those calcined at 600 °C. Dense pellets were prepared by sintering the green pellets at 1500 °C for 5 h with a ramp rate of 3 °C/min and naturally cooled in the furnace. The relative density of the sintered pellets was determined using the Archimedes' principle. Powder XRD analysis was performed on polished samples.

Electrodes were painted using a gold paste onto both sides of the pellets, and fired at 800 °C for 2 h. The pellets were placed in an alumina holder using a spring-clip arrangement between Pt current collectors. The electrochemical impedance spectroscopy (EIS) measurements were performed from 0.1 Hz to 10 MHz, using a Solartron 1260 impedance/gain phase analyzer, interfaced to a personal computer, and run through ZPlot® and Zview software (Scribner Associates, Incorporated); 10 points were taken per decade of frequency. The amplitude of the AC signal imposed on the samples was 10 mV. The EIS measurements were performed at controlled temperatures in the 225–700 °C range.

3. Results and discussion

The various complexes between $Ce(NO_3)_3$, $Gd(NO_3)_3$, and TEA were prepared in propan-1-ol. Yellowish powders were obtained, although the contents of Ce^{3+} and Gd^{3+} varied. The yellowish powders were precipitated when the complexes completely reacted in propan-1-ol for 3 h.

To obtain the ceramic powders, the complexes were calcined to remove the organic contents. The appropriate temperature for calcination was studied using TG/DTA measurements. Fig. 1, as an example, shows the TG/DTA curves of the complex for 10 mol% GDC. The broad endothermic peak, centered at ~100 °C on the DTA curve, was mainly caused by the loss of