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Synthesis and characterization of $Gd_{0.1}Ce_{0.9}O_{1.95}$ nanopowder via an acetic–acrylic method

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Abstract

Nanocrystalline $Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC) powders are successfully prepared by an acetic–acrylic method using acrylic acid, cerium acetate and gadolinium acetate as the starting materials. The polymeric precursors are characterized by means of TG/DTA, XRD and FT-IR, and the resultant powders are characterized by XRF, BET, SEM and particle size distribution (PSD) analysis. It is shown that the morphology of the oxide particles is dependent on the preparation conditions such as molar ratio of acrylic acid to metallic ions (L/M) and the sort of surfactant. High purity, single phase, homogeneous, nanocrystalline GDC powders with slight aggregation are obtained using ethylene glycol as surfactant, $L/M=0.5$ and heat treatment above 600 °C. The low application amount and high effect of acrylic acid is attributed to the co-operation of carboxyl group and ethylenic bond. The electrical conductivity of the sintered GDC pellet is 0.053 Scm^{-1} in air at 750 °C. The present work indicates that the acetic–acrylic method is a relatively green method without any NO_x to synthesize high performance GDC powders.

Keywords: C. Ionic conductivity; E. Fuel cells; Acetic–acrylic synthesis; Gadolinium doped ceria

1. Introduction

Solid oxide fuel cell (SOFC) is one of the cleanest, most efficient and versatile technology for the chemical to the electrical energy conversion. Among all the oxygen ion conductors, yttria stabilized zirconia (YSZ) is the most commonly used for the SOFCs. This typical material requires a high operation temperature which leads to several technological problems, such as mechanical instability, reduced lifetime and undesirable reactions between the cell components. Doped ceria has more oxygen vacancies and it shows a higher oxide ionic conductivity than YSZ. In the rare-earth doped ceria, the highest conductivities are observed for $Ce_{1-x}Gd_xO_{2-x/2}$(GDC).

Various methods have been used to prepare nano-sized doped ceria, such as the sol–gel [1–4], microwave-combustion [5–9], acrylamide polymerization [10,11], polymer-pyrolysis [12], microemulsion [13,14], homogeneous precipitation [15,16], hydrothermal [17,18] and mechanochemical [19,20].

The most common used method is the combustion method, which starts with the metal nitrates and the citric acid. The powders prepared by the combustion method are more homogeneous, have fewer impurities and higher surface areas. Dong et al. [5] tried to induced a polymer hydrogel assisted combustion synthesis to produce highly crystalline ceramic nanoparticles using cross-linked polyacrlyamide hydrogel as the fuel. However, during the combustion process, the volume expands and sometimes even the precursor burns. To our experience, this will make the process uncontrollable and some problems involves when it comes to scale up.

Liu et al. [12] induced a polymer-pyrolysis route to synthesize nanocrystalline materials with high yield and large scale. The simultaneously polymeric precursors were made by in situ polymerization of the mixed aqueous solution of acrylic acid in the presence of metal nitrates, with $(NH_4)_2S_2O_8$ as the initiator. They believed the metallic ions were bound by the strong ionic bonds between the metallic ions and carboxylate ions in a polymeric chain or between the polymeric chains. However, it should be mentioned that the pretreatment process in the polymer-

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pyrolysis method can produce some NO_x due to the decomposition of the residual NO_3^-.

The acrylamide polymerization process in the synthesis of highly dispersed mixed oxides has been described by Sin [21]. Tarancón [11] chose nitrate salts to synthesize ultrafine and highly homogeneous powder of $Gd_{0.2}Ce_{0.8}O_{1.9}$. In this powder synthesis process, the monomers of acrylamide ($CH_2{=}CHCONH_2$), the initiator and the cross-linker were dissolved to form the chains of polyacrylamide. During the polymerization process, an auxiliary three-dimensional (3D) tangled network was formed by polyacrylamide gel, in a solution of the appropriate cations. They believed the complexation of cations by acrylamide significantly decreased the rate of the polymerization reaction and impeded the formation of the 3D tangled network. In order to avoid metal-complexation by acrylamide, they chelated the cation in solution by EDTA. This method can be used to synthesize ultrafine powders of a wide variety of ceramic materials with applicability in SOFC. However, it is known that the acrylamide is neurovirulence and the high toxicity level of acrylamide forced them to search for an alternative monomer for gel constitution.

In this study, we report for the first time the preparation of nanocrystalline GDC via an acetic–acrylic method without using any nitrate materials. The pyrolysis process was studied by means of TG/DTA, XRD and FT-IR. The synthesis conditions of the molar ratio of acrylic acid to metallic ions and surfactants were also optimized. Furthermore, we studied the mechanism of acrylic acid using the FT-IR spectra and SEM. The electrical property of the material was also studied by a frequency response analyzer.

2. Experimental procedure

2.1. Powder synthesis

Cerium acetate hydrate ($Ce(CH_3COO)_3 \cdot 4H_2O$, 99.99%, Aladdin) and gadolinium oxide (Gd_2O_3 99.99%, Aladdin) were used as metallic precursors. Acetic acid and acrylic acid were used as solvent and polymerized monomer in the synthesis of $Ce_{0.9}Gd_{0.1}O_{1.95}$. The synthesis of the powders by the acetic–acrylic method is shown as a flow chart in Fig. 1. A stoichiometric amount of Gd_2O_3 was dissolved in acetic acid and cerium acetate hydrate was added subsequently to obtain a mixed acetic aqueous solution. Different amounts of acrylic acid with the molar ratio of acrylic acid to metallic ions (L/M) of 0, 0.5, 1 and 4 were added to the solution respectively to study the influence on morphology. Lastly, 0.5 g of different surfactants PEG, PVA, PVP and EG were added to study its effect on the synthesis process.

The solution was heated and stirred in a water bath at the temperature of 80 °C for 5 h to evaporate the water. Then the white gel-like precursors were dried at 110 °C for 12 h and 250 °C for 6 h later. Finally, the obtained yellow ash was heated in a muffle furnace at different temperatures to investigate its properties of structure and sintering.

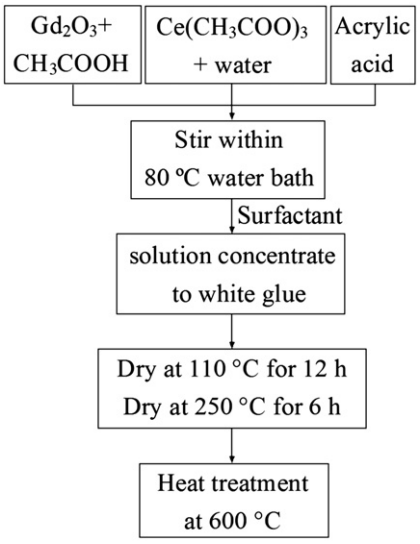

Fig. 1. Flow chart of GDC synthesis by the acetic–acrylic method.

2.2. Powder characterization

To study the thermal decomposition process and the phase evolution, the gel precursor was dried in a vacuum oven at 110 °C. TG/DTA analysis at the temperature range of 30–900 °C was carried out with a heating rate of 5 °C min^{-1} in air. The room temperature X-ray powder diffraction (XRD) data were collected on a diffractometer with Cu-Ka radiation. Data were recorded at a step of 0.02° s^{-1} in the range of 2θ from 10° to 90°. The structural feature of the polymeric GDC precursor and reactants were characterized by Perkin-Elmer FT-IR spectroscopy using KBr pellet method in the range of 500–4000 cm^{-1}. The purity of the synthesized GDC powders was measured by XRF (Rigaku ZSX Primus II). Specific surface areas of GDC powders were measured by the Brunauer Emmett Teller (BET) isotherm technique with nitrogen adsorption using a Micromeritics ASAP 2020M physisorption analyzer. Particle size distribution (PSD) analysis was made by Zatasizer Nano ZS Malvern Instruments Ltd. (UK). The morphologies of the synthesized powders and pellets were characterized by means of scanning electron microscopy (SEM) using a Hitachi S-4800 microscope.

The resultant GDC powders were pressed into a pellet of 8 mm diameter and 1.0 mm thickness under a pressure of 300 MPa, and then sintered at 1500 °C for 5 h. The impedance was measured using a frequency response analyzer (Soltron 1260) over a frequency range from 0.1 Hz to 10 MHz at 400–800 °C in air. The ionic conductivity σ and the activation energy E_a were derived from the impedance data.

3. Results and discussion

To study the chemical reactions of the gel precursor occurred in the pyrolysis process, TG/DTA, FT-IR, and XRD analysis of the precursor were conducted. The TG/DTA results of the GDC precursors dried in a vacuum