Synthesis and Characterization of La\(_{0.75}\)Sr\(_{0.25}\)Cr\(_{0.5}\)Mn\(_{0.5}\)O\(_{3-\delta}\) Nanoparticles Using a Combustion Method for Solid Oxide Fuel Cells

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ABSTRACT

La\(_{0.75}\)Sr\(_{0.25}\)Cr\(_{0.5}\)Mn\(_{0.5}\)O\(_{3-\delta}\) (LSCM) perovskite nanoparticles for use as anode material in intermediate temperature solid oxide fuel cells (IT-SOFCs) were synthesized using 3,3',3"-nitrilotripropionic acid (NTP), citric acid and oxalic acid as carriers via a combustion method. The influence of the carrier on phase and morphology of the obtained pristine products was characterized using X-ray diffraction (XRD), thermal gravimetric analysis (TGA), and scanning electron microscopy (SEM). XRD results showed, that the LSCM had rhombohedral symmetry with R-3c space group; a single phase LSCM perovskite formed after calcination of fired gel at 1200°C for 7 h. Scanning electron microscopy analysis of the pristine powders showed spherical shape and particle sizes in the range of 50 - 500 nm.

Keywords: Nanoparticles, Combustion method, Morphology, Carriers

1. Introduction

A fuel cell is an electrochemical device that converts chemical energy of fuels (hydrogen, methane, butane or even gasoline and diesel) into electrical energy by exploiting the natural tendency of oxygen and hydrogen to react. Fuel cells are simple devices containing no moving parts and only four functional components namely cathode, electrolyte, anode and interconnect. Solid oxide fuel cells (SOFCs) are considered to be among the most versatile power production facilities. Their unique characteristics include extreme efficiency, significant energy conversion rate with a wide range of fuels and pollution-free operation. On the other hand high operating temperature (about 1000°C) of the SOFC results in problems including difficult sealing between cells with flat plate configurations and thermal expansion mismatches between components. In addition, the high operating temperature places rigorous constraints on materials selection and results in difficult fabrication processes [1].

Recently, perovskite based conducting oxides, such as substituted lanthanum chromites or lanthanum manganates and strontium titanates, received great attention as alternative anode materials for solid oxide fuel cells [2]. Particularly, (La\(_{0.75}\)Sr\(_{0.25}\))\(_{1-x}\)Cr\(_{0.5}\)Mn\(_{0.5}\)O\(_{3-\delta}\) perovskite phase (LSCM) has been considered as a capable anode material for SOFCs due to its electrocatalytic/catalytic activity for oxidation of methane fuel in the absence of steam, reduced carbon deposition, and high durability against sulfur poisoning and good electrical properties [3,4]. Predominantly, this composition of LSCM has shown good stability in fuels and in air, and has good resistance towards carbon deposition and low polarization resistance when used with hydrocarbon fuels [5]. LSCM can also be used as a cathode, thus facilitating fuel cells with a symmetrical structure (LSCM/electrolyte/LSCM) [6,7].

Up till now, various chemical methods were reported in the literature for the synthesis of LSCM powders, for example, glycine nitrate method [3], EDTA (ethylenediaminetetraacetic acid) chelating method [8,9], combustion synthesis [7,10], solid-state reaction [4,6,11-15], gel-casting [16,17] and co-precipitation method [18]. The solid-state
method has some disadvantages such as high temperature (above 1300°C) and long duration of synthesis of LSCM and non-homogeneity in particle size and low purity [19]. However, to synthesize homogeneous fine particles of pure phase LSCM powders requires low temperature and short duration of synthesis. The solution combustion method is suitable to synthesize nanosize LSCM particles with good homogeneity [20]. The present work reports on the synthesis of nanostructured La0.75Sr0.25Cr0.5Mn0.5O3−δ (LSCM) perovskite by a combustion method using 3,3',3''-nitrilotripropionic acid, oxalic acid and citric acid as carriers.

2. Experimental

Nanostructured La0.75Sr0.25Cr0.5Mn0.5O3−δ (LSCM) perovskite anode material was synthesized by a combustion technique. Three batches of LSCM solutions are prepared with stoichiometric amounts of lanthanum nitrate (La(NO3)3·6H2O), strontium nitrate (Sr(NO3)2), chromium nitrate (Cr(NO3)3·9H2O) and manganese nitrate (Mn(NO3)2) in distilled water under constant stirring. First, a stoichiometric amount of citric acid (C6H8O7·H2O) and 15 ml ethylene glycol are added as carriers. The react and mixture during the formation of perovskite phase, and also the completion of the nucleation by the rearrangement of atoms by short distance diffusion. The fast combustion process might not be of the help to overcome the lattice energy, which is required for the formation of the perovskite phase in this combustion process. The large heat released during combustion might be of the help to overcome the lattice energy, which is required for the formation of the perovskite phase, and also the completion of the nucleation by the rearrangement of atoms by short distance diffusion. The fast combustion process might not be of help for the diffusion of atoms far from each other and hence the particle size of LSCM powder remained in the nanometer range [22].

In the synthesis of La0.75Sr0.25Cr0.5Mn0.5O3−δ (LSCM) perovskite nanoparticles the carriers (NT, oxalic acid and citric acid) help in obtaining a homogeneous mixture of the cations in a solution through forming metal complexes, they also help in the reduction of nitrates in a combustion process, releasing a large amount of heat. This is shown by an exothermic peak at 377°C on a DSC curve (Figure 2). During the solid-state reduction process, metal cations and oxygen anions stay in the react and mixture during the formation of perovskite phase in this combustion process. The large heat released during combustion might be of the help to overcome the lattice energy, which is required for the formation of the perovskite phase, and also the completion of the nucleation by the rearrangement of atoms by short distance diffusion. The fast combustion process might not be of help for the diffusion of atoms far from each other and hence the particle size of LSCM powder remained in the nanometer range [22].

Thermogravimetric analysis and differential scanning calorimetry (TGA-DSC) curves with NTP-assisted LSCM dried as a gel at 120°C are shown in Figure 2. The weight losses happen in three steps. The total weight loss

![Figure 1](link-to-figure1)  
**Figure 1.** XRD patterns of La0.75Sr0.25Cr0.5Mn0.5O3−δ (LSCM) perovskite phase nanoparticles.
was 2.1 mg from room temperature to 1300°C. The first weight loss is 0.33 mg in the temperature range 22°C - 236°C; this can be attributed to evaporation of water from the layers of LSCM. The second weight loss is 1.25 mg in the temperature range 236°C - 383°C and the third weight loss is 0.5 mg in the temperature range 383°C - 837°C. The second and third weight losses are attributed to decomposition of the carrier (NTP) and evaporation of structurally bounded water. The peaks located at about 295°C and 377°C are exothermic on the DSC curve due to decomposition of nitrates and organic matter and correspond to the second weight loss of 1.25 mg from about 236°C to 400°C as observed in the TGA curve.

To observe thermal effects above 350°C, different carrier-assisted LSCM samples were fired at 350°C for 1 h. Figure 3 shows TGA-DTA curves of the different carrier’s assisted LSCM samples. The total weight loss was 0.97 mg in NTP assisted LSCM, 0.39 mg in oxalic acid assisted LSCM, and 0.77 mg in citric acid assisted LSCM from room temperature to 1300°C. The first weight loss is 0.32 mg in NTP assisted LSCM in the temperature range 30°C - 490°C, whereas the first weight loss is 0.2 mg in the oxalic acid used LSCM in range 30°C - 338°C and the first weight loss is 0.25 mg in citric acid used LSCM in range 30°C - 334°C. The second weight loss is 0.9 mg in NTP used LSCM in the temperature range 490°C - 822°C, whereas the second weight loss is 0.42 mg in citric acid used LSCM in range 334°C - 688°C. The second weight loss was attributed to the reaction between the residual nitrate and carriers after the decomposition of the precursor and subsequent combustion of organic components.

The morphologies of La$_{0.75}$Sr$_{0.25}$Cr$_{0.5}$Mn$_{0.5}$O$_{3-\delta}$ perovskite phase nanoparticles (a) NTP-assisted, (b) oxalic acid assisted and (c) citric acid assisted.
4. Conclusions

La$_{0.75}$Sr$_{0.25}$Cr$_{0.5}$Mn$_{0.5}$O$_3$ (LSCM) perovskite phase nanoparticles were successfully synthesized by solution combustion method using different carriers (NTP, oxalic acid, and citric acid) after calcination of fired gel at $1200^\circ$C for 7 h. Scanning electron microscopy of the as-synthesized powders showed spherical particle shapes and sizes in the range of 50 - 500 nm (Figures 4(a) and (b)). The small size La$_{0.75}$Sr$_{0.25}$Cr$_{0.5}$Mn$_{0.5}$O$_3$ perovskite nanoparticles are very active, small size is also beneficial for decreasing the fabrication temperature of the anode film and enhancing the catalytic properties.

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