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Preparation and characterization of nano ceramic size $La_{0.5}Ni_{0.5}FeO_3$, and $La_{0.8}Sr_{0.2}CO_{0.2}Fe_{0.8}O_3$ cathodes for Solid Oxide Fuel Cells

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Abstract

Nanopowders of $La_{0.5}Ni_{0.5}FeO_3$(LNF), and $La_{0.8}Sr_{0.2}CO_{0.2}Fe_{0.8}O_3$(LSCF) were synthesized by glycine-nitrate combustion process using glycine and metal nitrates as the starting materials. Development of crystalline phases in the powders after heat treatments at various temperatures was characterized by X-ray diffraction (XRD). Single phase perovskites were obtained after heat treatment of the combustion synthesized LNF and LSCF nanopowders. Morphological properties of powders calcined at different temperatures were characterized by scanning electron microscopy (SEM). The dielectric measurements were carried out at room temperature as a function of frequency and composition. The experimental results reveal that dielectric constant decrease where as ac electrical conductivity increases as frequency increases.

Keywords: Nanopowder, glycine-nitrate, dielectric constant, electrical conductivity.

Introduction

In recent years the development of fuel cell technology has been rapid, and several types of fuel cell have been developed depending on the intended applications. One of the many types fuel cells available, the solid oxide fuel cell (SOFC) has shown considerable promise for a variety of applications. The main characteristic of solid oxide fuel cells is its ability to convert chemical energy directly into electrical power with high conversion efficiency and negligible pollution. Unfortunately, the cost of the current solid oxide fuel cell systems is still prohibitive for broad commercialization. To be economically competitive, both the cost of materials and the cost of fabrication for SOFC systems must be dramatically reduced. One effective approach to cost reduction is to reduce the operating temperature. If SOFCs can be operated 800-1000 ^{o}C for example, many components can be fabrication from much less expensive materials. Additional benefits of lower operating life, and increased potential for mobile applications and for cost-effective fabrication.[1-3]

The goal of this work was to synthesize nanopowders of electrode composition for applications as SOFC electrodes. A wide variety of methods have been synthesized powders such as solid state reaction, citrate method, hydrothermal, sol–gel thermolysis spray-drying, freeze-drying, co-precipitation. But these powders often lack in compositional uniformity, or sintered at high temperatures and for a long time. But Glycine-nitrate combustion method is another promising technique for the production ultrafine ceramic powders of complex compositions in a relative short time. The aim of the present work is the synthesize homogeneous LNF, and LSCF electrode nanopowders using the glycine-nitrate combustion process, because of its high-energy efficiency, fast heating rates, short reaction times, and high reaction temperatures. The process is also unique as all the reactants are mixed in the solution at the molecular level resulting in homogeneous reaction products and faster reaction rates.[2-7]

Experimental

The nano-crystalline LNF and LSCF powders were synthesized by a glycine-nitrate combustion process using glycine as the fuel for combustion process. The experimental procedure for the synthesis of electrodes is depicted as the flow chart is shown in Fig.1. In this method, required stoichiometric amount of nitrate were weighted and mixed with tripple distilled water in a glass beaker. A calculated amount of the glycine was dissolved in double triple distilled water. The glycine solution was slowly added into the mixed solution to form a transparent, homogeneous solution with heating and constant stirring for 30 min. According to the concepts used in propellent chemistry, the stoichiometry amount of the redox mixture used for the combustion reaction was calculated based on the total oxidizing(O) and reducing (F) valenices of the components which serve as the numerical coefficient for the stoichiometric balance to equivalent ratio was maintained at unity(O/F), so that the heat released by the combustion is maximum. The solution in the glass beaker was heated on a hotplate until self-sustaining combustion, and the black powder was obtained. The synthesized precursor was heated at 600 ^{o}C for 2 h to remove residue organic materials.

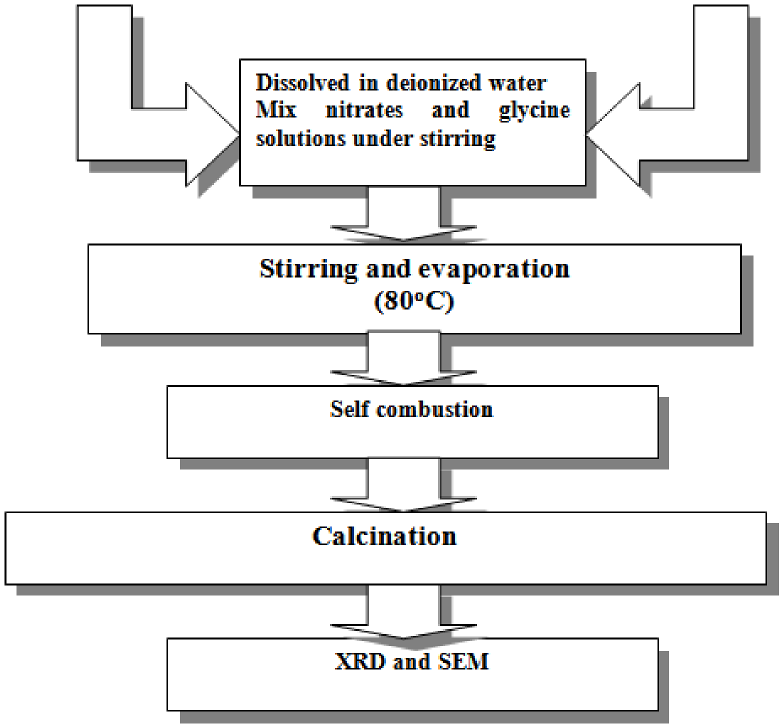

Fig.1. Flow chart for Glycine-Nitrate combustion synthesis of SOFC electrode nanopowders

LNF and LSCF were then mixed with polyvinyl alcohol as a binder and pressed into pellets of 10 mm diameter and thickness of 2–3 mm using a hydraulic press. The pelletized samples were finally sintered at different temperatures for 12 h in a programmable furnace.

The powders were characterized by XRD diffractometer (Philips, Model PW-1710) using Cu Kα radiation (λ = 1.5418 Å) for crystal structure analysis. The microstructure of sintered samples surface was observed using a scanning electron microscope (SEM; JEOL, JSM-5310). Silver paste was applied on the flat surfaces of the pellet for good ohmic contact.

The AC parameters such as capacitance (c) and dissipation factor (tan δ) of the samples were measured in the frequency range 100 Hz to 1 MHz using LCR meter (HP Model 4284 A). The variation of dielectric constant and loss tangent with room temperature were studied by recording these parameters at different frequencies (100 Hz to 1 MHz). The dielectric constant ($\acute{\varepsilon}$) was calculated using the relation:

$$\varepsilon = ct / \varepsilon_o A$$

where c is the capacitance of the pellet, t the thickness of the pellet, A the area of cross section of the pellet and ε_o is the permittivity of free space (8.854×10^{-12} F m^{-1}).

Results and discussion

LNF and LSCF synthesized powders were calcinated in air for 2h at different temperatures. X-ray diffraction pattern (XRD) for 700, 800 and 1000^{o}C heat treated LNF and LSCF powders are shown in Fig.2. It can be seen that the major peaks are well indexed and almost the same as orthorhombic perovskites of GdFeO3 with space group Pnma (LaFeO3 JCPDS 37-1493).

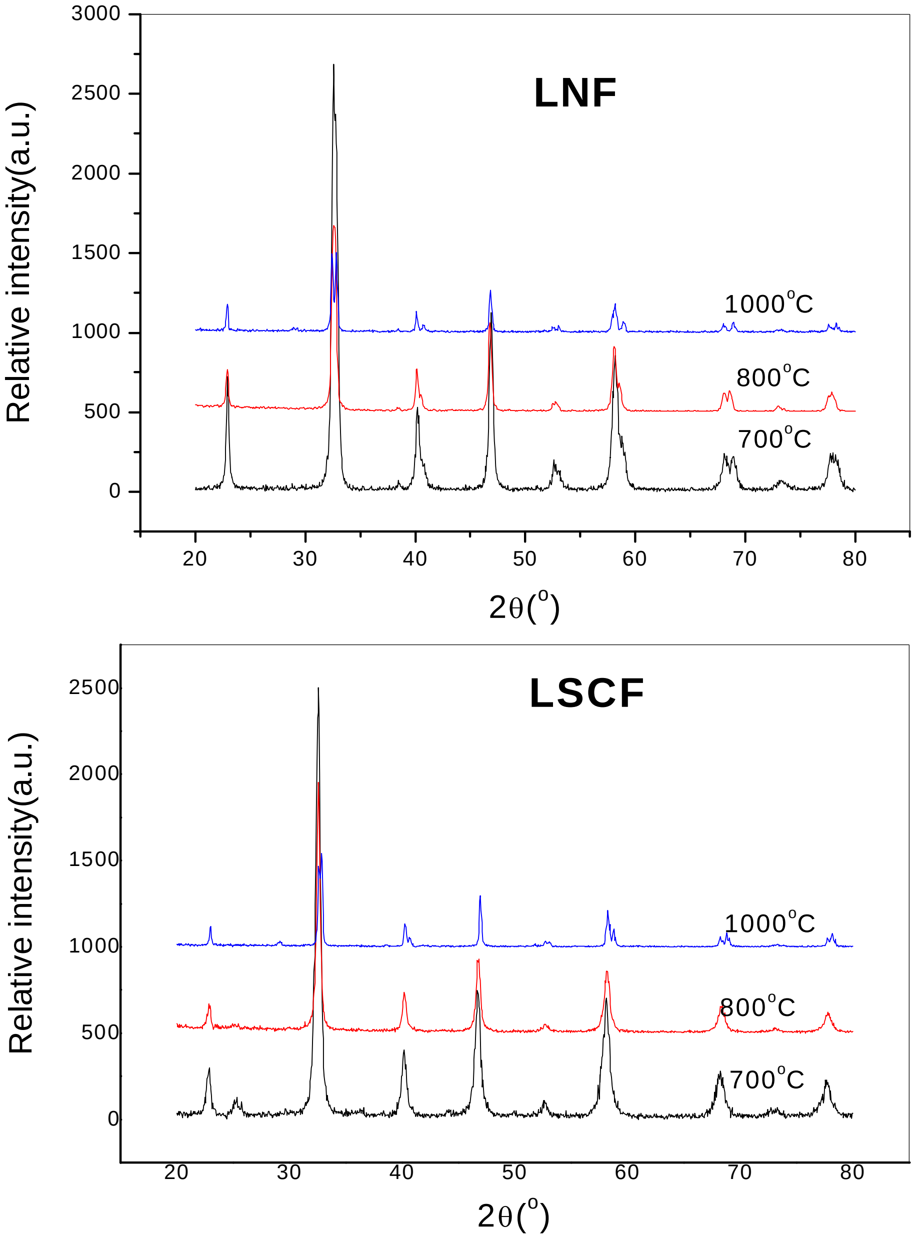

Fig.2. XRD patterns of powders synthesized by glycine-nitrate combustion method and powders sintered at different temperatures for 2 h: (a) LNF (b) LSCF

The SEM micrographs of LNF and LSCF powders made by glycine-nitrate combustion synthesis after that treatments at 1000 oC temperatures for 2 h in air is presented in Fig.3.

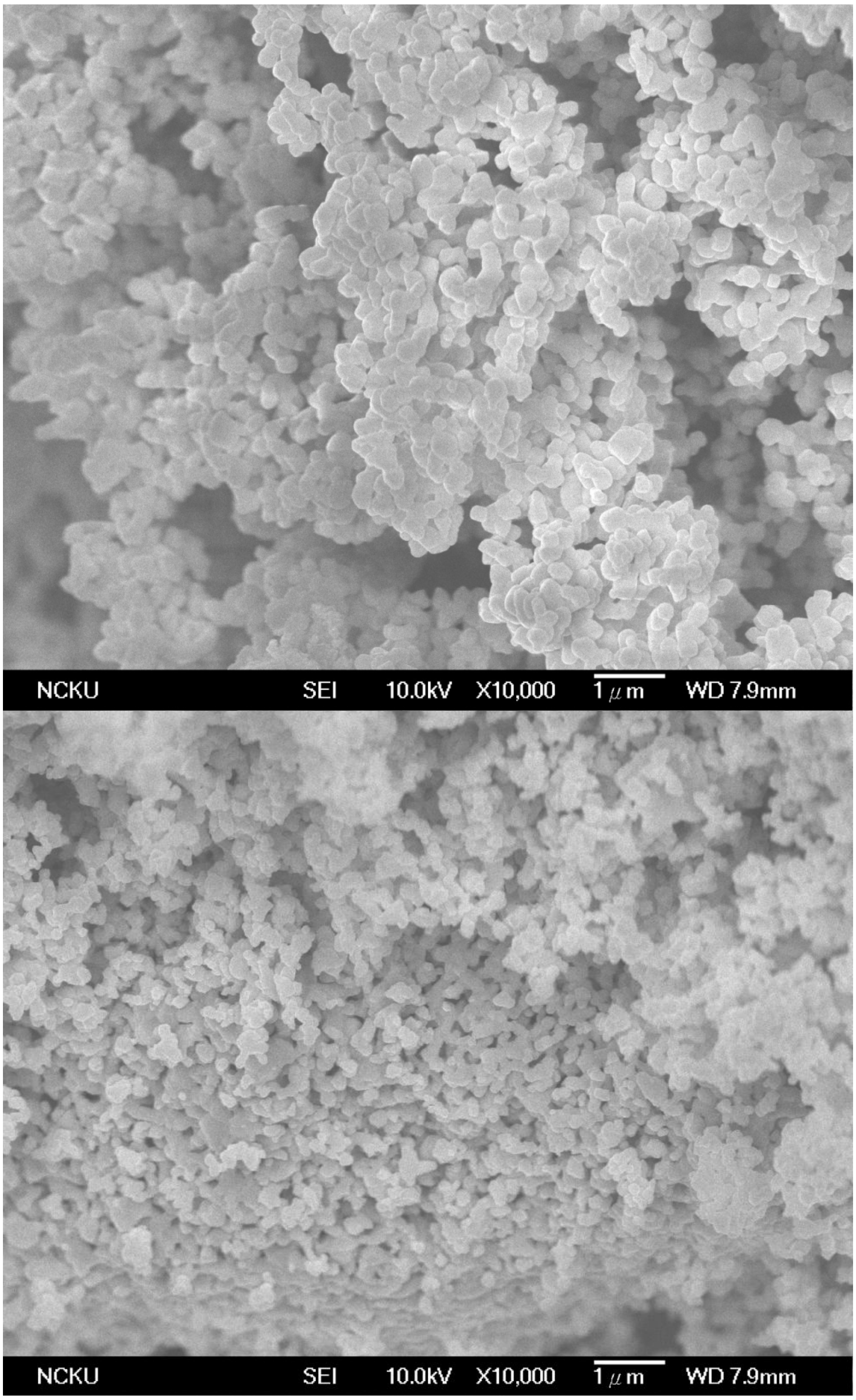

Fig.3. SEM micrographs of LNF and LSCF powders made by glycine-nitrate combustion synthesis after heat treatment at 1000 ^{o}C temperatures for 2 h.

The particle size of samples calcinated at 1000 oC, the structure highly porous, which indicated the typical cathode structure for solid oxide fuel cell.

The variation of dielectric constant with frequency at room temperature is shown in Fig.4 . From the figure it can be seen that the dielectric constant decreases with increase in frequency reaching constant value at higher frequencies. The variation of ac electrical conductivity with frequency at room temperature is shown in Fig.5. It can be seen that the ac electrical conductivity increases with increase of frequency.[8-9]

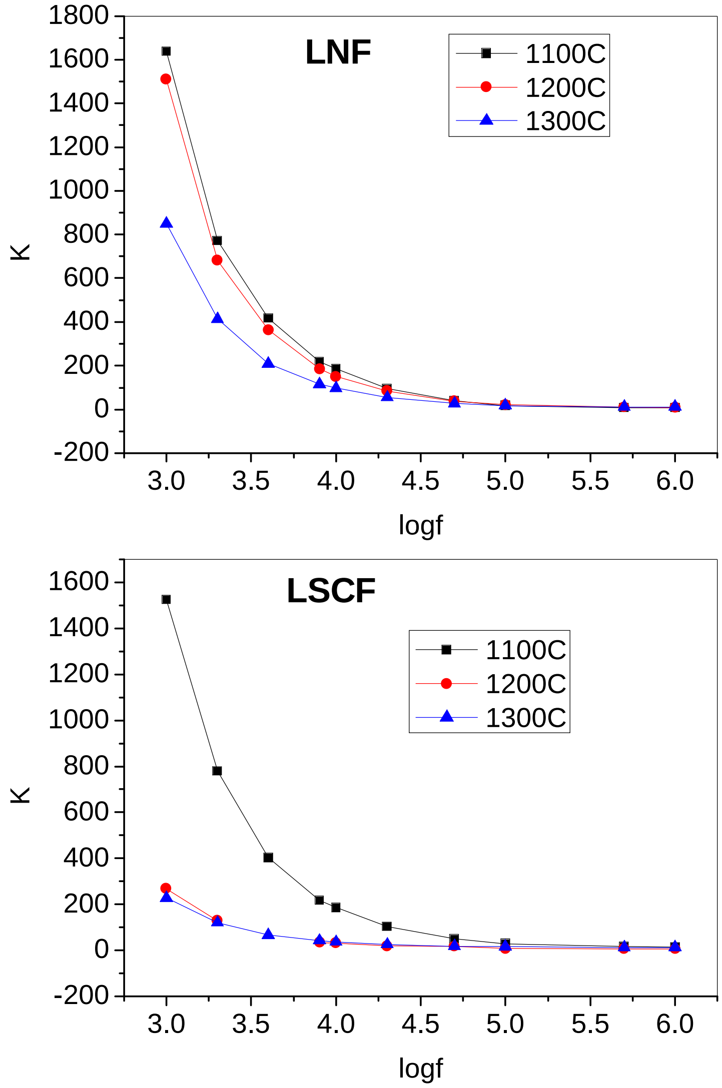

Fig.4. Room temperature dielectric constant of LNF and LSCF cathode as a function of frequency

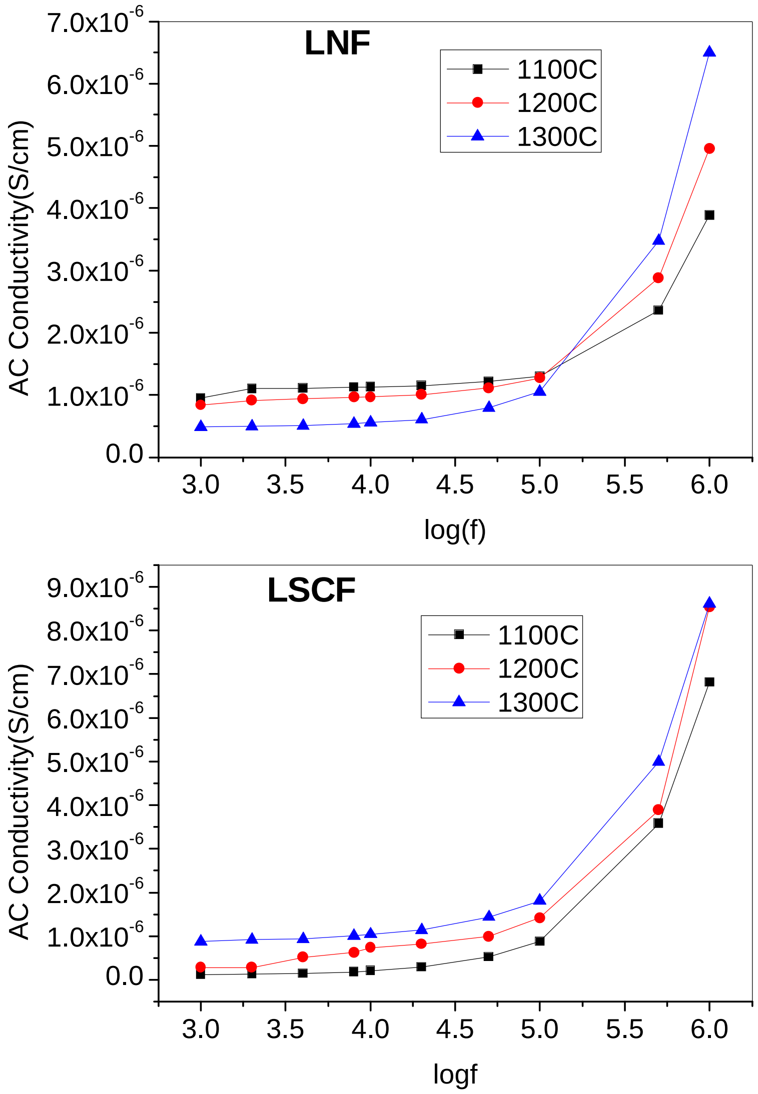

Fig.5. Room temperature AC conductivity of LNF and LSCF cathode as a function of frequency

The phenomenon of the conductivity dispersion in solids is generally analyzed using jonschers law [10] $\sigma(\omega)=\sigma_0+A\omega^n$, where σ_0 is the DC conductivity fr a particular temperature, A is a temperature dependent constant and n is the power law exponent which generally varies between 0 and 1 depending on temperature. The exponent n represents the degree of interaction between mobile ionics with the lattice around them. The prefactor A determines the strength of polarizability.

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Conclusions

The $La_{0.5}Ni_{0.5}FeO_3$(LNF), and $La_{0.8}Sr_{0.2}CO_{0.2}Fe_{0.8}O_3$(LSCF) nano ceramic powders for cathodes were successfully prepared by glycine-nitrate process. SEM images of LNF and LSCF powders indicate the presence of highly porous particles, which is beneficial for intermediate temperature SOFC. The XRD results show that the single perovskite LNF and LSCF phase completely formed after heat treatment at 800 oC for 2 h in the air. The dielectric constant decrease while ac conductivity increases as the frequency increases for all the samples.

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