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Original Research Paper

Synthesis of Ni-doped $LaSrMnO_3$ nanopowders by hydrothermal method for SOFC interconnect applications

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ABSTRACT

Ni-doped lanthanum strontium manganite (LSMN) nanopowders, $La_{0.7}Sr_{0.3}Mn_{1-x}Ni_xO_3$ ($0.05 \leq x \leq 0.3$) were synthesized at 150 °C for 8 h by hydrothermal reaction as a function of Ni doping concentration. The SEM analyses suggested that the calcination treatment influenced the morphology of the nanopowders. The calcined nanopowders at 1300 °C had agglomerated spherical structure of 44–77 nm. Meanwhile, the XRD studies revealed that the nanopowders have single crystalline phase over the range x = 0.05–0.2. In addition, the LSMN nanopowders were sintered at elevated temperatures, 1250–1350 °C to examine their electrical conductivity for solid oxide fuel cell (SOFC) interconnect applications under actual SOFC working condition. Their electrical conductivity gradually increased to 90.05 S/cm with Ni doping concentration x = 0.2, which were sintered at 1300 °C. These results suggest $La_{0.7}Sr_{0.3}Mn_{0.8}Ni_{0.2}O_3$ displays a good performance as an optimal composition of the LSMN.

1. Introduction

A solid oxide fuel cell (SOFC) has become of great interest as an economical, a clean and efficient alternative for electrochemical energy conversion devices. In comparison with conventional energy generations, the SOFC offers several advantages such as higher energy conversion efficiency, potential for cogeneration and low emission of environmental contaminants [1,2]. However, SOFCs need high operating temperature to maintain good performance. Thus, it is considered cost-effective to lower the operating temperature for commercialization of the SOFCs and for improvement of the durability. In addition, a formation of large reaction area and dense films has been suggested to improve the SOFC performance and to have high thermal endurance, respectively.

An SOFC unit cell consists of cathode, anode, electrolyte and interconnect. The SOFC interconnect performs electrical connection to each unit cell and separation between cathode and anode. Accordingly, interconnect materials have several qualifications which require chemical stability in oxidation-reduction at high temperature, high electrical conductivity, similar thermal expansion with other components, low reaction with other components, and high density [3]. However, a dilemma of SOFC is its poor performance at the relatively low operating temperatures to sustain the working performance for long time.

Lanthanum strontium manganite (LSM), $La_{1-x}Sr_xMnO_3$ ($0.2 \leq x \leq 0.3$) which has perovskite structure ABO_3, is one of preferable materials for SOFC interconnects. LSM is well known to have high electrical conductivity, compatibility with other cell components and high chemical stability in oxidation atmosphere at the high SOFC working temperature [3]. However, a drawback of LSM is its poor chemical compatibility with zirconia electrolyte below sintering temperature, 1300 °C [3]. In addition, LSM is not suitable for operating at medium-low temperature below 800 °C. Therefore, the perovskite structures have been tuned in order to have a higher electrical conductivity in LSM at the relatively low operating temperature [4,5], Mostly, components and compositions of B-site in the perovskites have been tuned to improve the electrical conductivity of the primitive LSMs [6]. In general, doping of the transition metal can lead to increase of charge carrier concentration in oxide materials. As a result, Cr, Co and Ni have been suggested to be the representative substitution on the B-site of the LSM [7,8]. However, it was revealed that the effects of Co and Ni doping on LSMs are dependent on the compositions of lanthanum and strontium in the LSMs [7,8]. Meanwhile, Co doping [9–11], and Cu-doped double perovskites [12,13] have been attempted to elevate electrical conductivity of the LSMs. Despite the failure in Ni doping on $La_{0.5}Sr_{0.5}MnO_3$ [7], the effect of Ni doping on $La_{0.8}Sr_{0.16}MnO_3$ was investigated as a function of Ni amount in the LSM [8,14].

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Unfortunately, the increase of Ni doping did not lead the LSM to any improvement in the electrical conductivity because of decrease in the grain surface area [14]. Among the controversy in the effect of Ni doping, we recently demonstrated that electrical conductivity of LSM is restricted to strontium doping limitation, suggesting $La_{0.7}Sr_{0.3}MnO_3$ as the optimal composition for LSM of high electrical conductivity [15]. In addition, we note there have been so far no report on Ni-doped LSMs for SOFC interconnect applications.

Considering preparing nanostructured SOFC components, there are several techniques based on solution chemistry such as glycine nitrate process [16], sol-gel process [17], coprecipitation [18], hydrazine method [19] and hydrothermal synthesis [20]. These techniques have been attempted for the preparation of highly homogeneous and fine powders of the perovskite oxide materials. These chemical processes, however, involve subsequent calcinations at high temperature, heterogeneous crystal and agglomeration. On the other hand, hydrothermal method is easy to control the particle size and shape, and the reaction occurs at low temperature under high pressure [15].

In this study, we employ the composition of $La_{0.7}Sr_{0.3}MnO_3$ as a Ni-doped LSM source to improve the electrical conductivity of the LSM for ceramic interconnects in SOFC. The Ni-doped LSM, $LaSrMnNiO_3$ (LSMN) nanopowders are synthesized at a relatively lower temperature by hydrothermal method. The physical properties and the phase purity of the synthesized nanopowders are characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD) analyses, respectively. XRD results show that the nanopowders have perovskite structures. Finally, the thermal behavior and electrical properties are investigated.

2. Experimental procedures

2.1. Hydrothermal synthesis and sintering

The starting materials were reagent grade $La(NO_3)_3{\cdot}xH_2O$ (Sigma Aldrich, USA), $Sr(NO_3)_2$ (KANTO Chemical, Japan) and $Mn(NO_3)_2{\cdot}xH_2O$ (Sigma Aldrich, USA). 3.5 M KOH (OCI Company, Korea) was chosen as a precipitant. Also, as a doping material, a reagent grade $Ni(NO_3)_2{\cdot}6H_2O$ was purchased from Sigma Aldrich (USA). The $La_{0.7}Sr_{0.3}Mn_{1-x}Ni_xO_3$ nanopowders were prepared at 150 °C for 8 h under hydrothermal condition. We chose the stoichiometric concentration of Ni from x = 0.05 to 0.3. As shown in Fig. 1, the starting and doping materials were added slowly in deionized water with precipitant KOH. The mixture was stirred for 1 h following with ultrasonic treatment for 30 min. The treated mixture was transferred into a Teflon container in an autoclave (Easy type, ILSHIN Autoclave, Korea). Then, the autoclave was heated up to 150 °C and the reaction was carried out for 8 h. After the hydrothermal reaction, slurry was washed with deionized water by using a centrifuge (FLETA5, Hanil, Korea) at 2000 rpm. The concentrated slurry was dried in an oven at 100 °C for 6 h. The dried powders were grinded by a mini mill (pulverisette23, FRITSCH, Germany). Subsequently, the milled powders were calcined at from 600 °C to 1300 °C to rule out the crystal impurity.

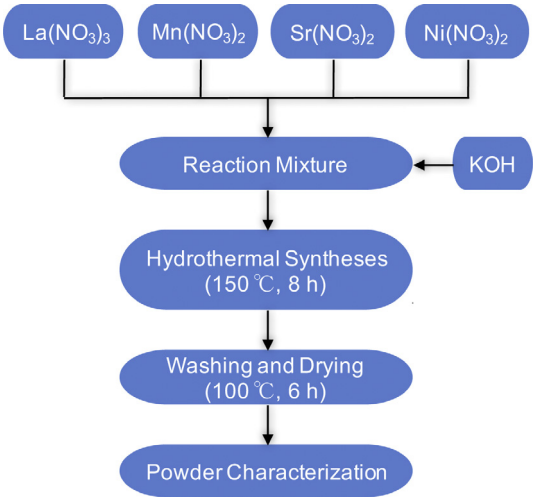

Fig. 1. A schematic view of hydrothermal synthesis of Ni-doped lanthanum strontium manganites.

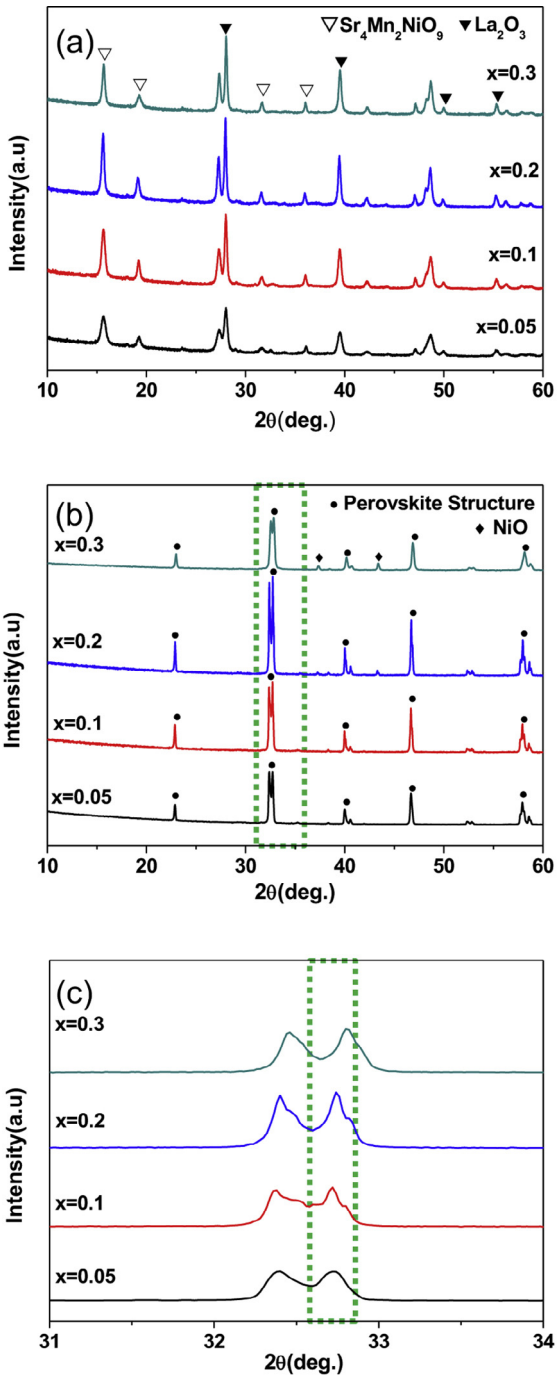

Fig. 2. XRD patterns of $La_{0.7}Sr_{0.3}Mn_{1-x}Ni_xO_3$ ($0.05 \le x \le 0.3$) nanopowders (a) before and (b), (c) after calcinations at 1300 °C for 3 h. The peaks in the dotted line of (b) are magnified in the dotted line of (c).

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