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STRUCTURE, ELECTRICAL PROPERTIES, AND APPLICATION POSIBILITY AS SOLID OXIDE FUEL CELLS CATHODE MATERIALS OF $(La_2NiO_{4\pm\delta})_{1-x}(BaTiO_3)_x$(x=0.0-0.5) COMPOSITES

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ABSTRACT

$(La_2NiO_{4\pm\delta})_{1-x}(BaTiO_3)_x$ (LNO/BTO), x=0.0, 0.05, 0.2, 0.3, 0.5 composites were prepared and investigated in structure and electrical properties. Single phase $La_2NiO_{4\pm\delta}$ component was obtained by sintering at 1000 ^oC during 12 h in air. Electrical conductivity was measured by 4-point probe method in wide temperature region above room temperature. Experiment showed that the highest conductivity was obtained in x=0.3 composite sample. Glass shell-nanocrystallite core structure of grains plays important role for this conducting enhancement. Conducting behavior of composites change from metal to semiconductor in the temperature interval of 400 to 700 ^oC. The LNO/BTO systems with acceptable electrical conductivity in such temperature interval are suitable for making cathode materials in solid oxide fuel cells.

Keywords: cathode, Solid Oxide Fuel Cells, LNO, BTO.

1. INTRODUCTION

At present time, research on proton conducting (PC) solid oxide fuel cells (PC-SOFC) operating in the temperature region closed to the room temperature, involves much attention of investigators. There are several conducting compounds potentially to be used as cathodes materials of PC-SOFC. The first one is single-phase mixed electron – proton conductor and the other is composite having combined proton-electronic or mixed oxygen ion/electronic conductivity [1]. Single phase perovskite La_2NiO_4 (LNO) and other most Ruddlesden-Popper series $La_{n+1}Ni_nO_{3n+1}$ (n = 2 and 3) have good oxide-ion conductivity, and are suitable cathode materials for intermediate temperature (650 - 800 ^0C) SOFC [2]. Authors of [3] found the optimum content for the composite SOFC cathode, which consists of 70 % $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) and 30 % volume percent of LNO. Single cell with this cathode gives an acceptable power density 479 $mWcm^{-2}$ at 800 ^{0}C. Doped LNO is also promising cathode materials for SOFC [4].

The aim of this research is to study other $(La_2NiO_{4\pm\delta})_{1-x}(BaTiO_3)_x$ (LNO/BTO) composites which may be used as cathode materials for lower temperature (<600 ^{0}C) SOFC. Donor-doped polycrystalline BTO and BTO-based materials present positive thermoresistive coefficient effect (PTCR) with low resistivity below 130 ^{0}C (see [5]). Electrical conductivity of BTO strongly depends on oxygen defects at grain surfaces [6], BTO constituent in composite can improve oxygen-ion and total conductivity.

Considering both advantages of BTO and LNO, composites $(LNO)_{1-x}(BTO)_x$ with x = 0.0, 0.1, 0.2, 0.3, 0.5 core-shell like structure were synthesized by the procedure described in [7].

2. EXPERIMENTAL

The BTO component of composites was manufactured by hydrothermal method. Stoichiometric barium titanium chlorine was mixed and dissolved with potassium hydroxide solution at pH equal to 12-13. Then, the homogeneous solution was pulled in thermal-bottle and heated at 150 ^{0}C for 7 hours. After exclusion of chlorine, the powder BTO sample was obtained. The LNO component was synthesized by sol-gel chemical method. All different nitrates were mixed in mole ratio. After that, citric acid was added and heated at 80 ^{0}C until obtained gel. In next step, the gel was burned at 500 ^{0}C for 2 hours. Then, the obtained powder was subjected to ball- milling to get optimized in size, and sintered at 1000 ^{0}C for 12 hours in air. The composite LNO/BTO was synthesized by chemical method where BTO powder was added in the LNO synthesis processes in order to get BTO grains covered by LNO. Before sintering at the same 1000 ^{0}C for 12 hours in air, the powder was pressed in pellets under pressure of 100 MPa, and re-pressed under hydrostatic pressure of 100 MPa to get more homogeneous samples.

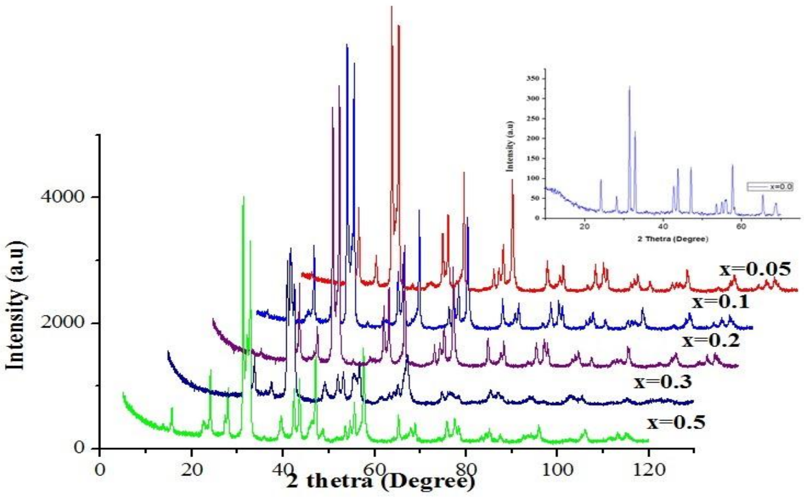

Figure 1. XRD patterns of LNO/BTO composites (x = 0.05, 0.1, 0.2, 0.3, 0.5) and LNO powder (inset) sintered at 1000 ^{0}C for 12 h.

Crystalline structure of all samples was examined by X-ray diffraction (XRD: Rigaku SmartLab). Structure and morphology of particles were analyzed by scanning electron microscope (SEM-JEOL). The varying oxygen content on temperature was determined by thermo-gravimetric analysis from room temperature to 800 ^{0}C in flowing air with the rate 10 ^{0}C/min. High temperature electrical properties were studied by four-probe technique in air from room temperature to 900 ^{0}C. The samples prepared for experiment have rectangular shape with 10 mm x 5 mm x 2 mm size. Electrodes were made by platinum paste on the clean surfaces of samples.

3. RESULTS AND DISCUSSION

XRD patterns of different powders: LNO, BTO, and composites LNO/BTO with x=0.0, 0.1, 0.2, 0.3, 0.5 are presented in Figure 1. XRD data analysis shows LNO, BTO are single phase. There is no trace of other phases and LNO's structure is orthorhombic like that given in [7]. It is clear to see diffraction peaks of LNO and BTO in composites. Incorporation of BTO and LNO in core-shell like structure is especially pointed in [8]. Grain size and morphology of powder samples can be observed in SEM images.

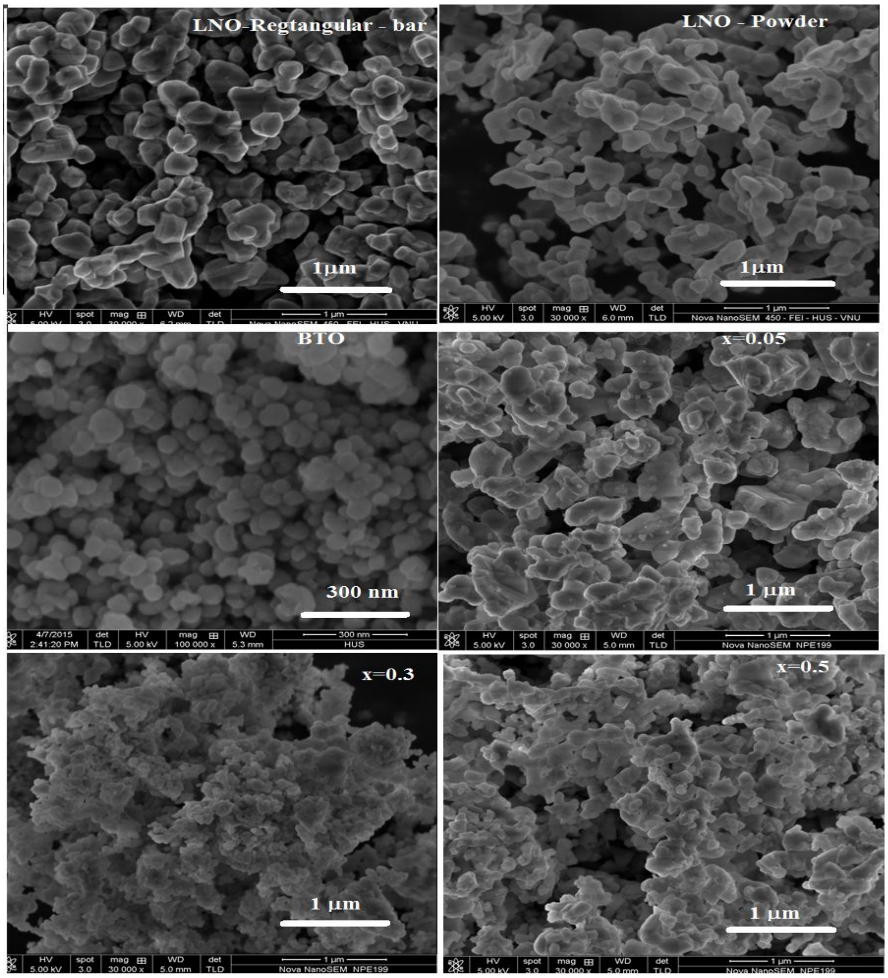

Figure 2. The SEM images of LNO bar (upper left), LNO powder (upper right), BTO and LNO/BTO composites (x = 0.05, 0.3, 0.5).

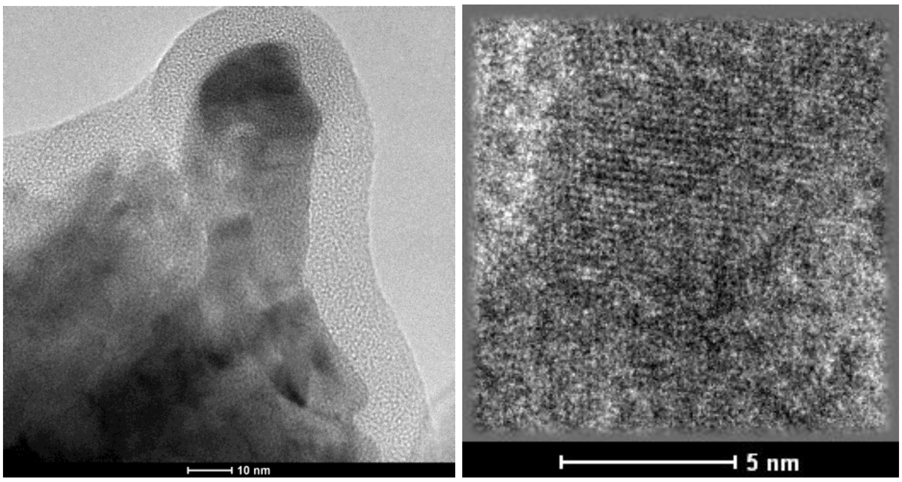

Figure 3. HR-TEM images of composite samples.

Figure 2 gives SEM images of BTO, LNO/BTO (x= 0.05, 0.3, 0.5) composites, LNO bar, and LNO powder. There is no difference between morphology and particle size of powder and bar LNO samples. Grain size distribution is very similar for composite samples and grain size decreases with increasing of BTO fraction from x = 0.05 to x = 0.3 but no further essential decrease for large BTO (x=0.5) content. SEM images for these three composite samples show additional morphology of core-shell like structure given in [8] where BTO is covered by LNO in grains.

Figure 3 shows core-shell like structure of one typical grain of LNO/BTO (x=0.05) composite. The shell is amorphous (or glass) and the core consists of LNO and BTO nano-crystallites (see also [8]). This special structure of glass-ceramic semiconductor nano-composite is essential for electron hopping process. Figure 4 shows the result of thermo-gravimetric analysis under air for LNO. It is clear to see few percent of the mass loss when temperature varies from 100 ^{0}C to near 600 ^{0}C and gradual change in the interval 600- 800 ^{0}C. This mass loss is related with changes in oxygen stoichiometry because of no changes in weigh concerning volatile lanthanum species. This oxygen nonstochiometry plays impotant role in conducting behavior of materials.

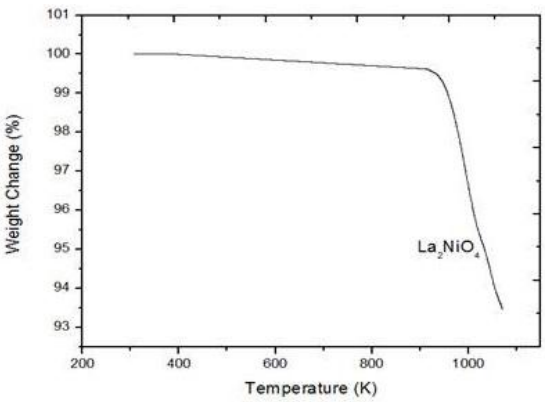

Figure 4. Thermo-gravimetric analysis in air for LNO.

Temperature dependence of electrical conductivity for LNO and composites LNO/BTO (x = 0.0, 0.05, 0.3, 0.5) is shown in Figure 5. One sees that more addition of BTO enhances feature of metal to semiconducting transition in LNO/BTO composite. The more interesting effect is the increase of BTO fraction from x=0 up to x=0.3 increases conductivity of composite sample more than 20 times in the temperature region lower than 400 ^{0}C. This is essential improvement of composite sample conductivity comparing with bare (x=0) one, which can be used for different purposes including materials for low temperature SOFC cathode.

Electrical conductivity of LNO /BTO composite is strongly depended on it grain structure. The glass shell- nanocrystallite core grain structure makes electron's hopping process more easily and enhances conductivity up to favorable BTO concentration (x=0.3). The situation here is similar to the case of enhancement of electrical conductivity of barium titanate based glass- ceramic nano-composites discovered in [9].

Although the absolute value of conductivity of samples is still low, but one can improve it by variation of the sintering temperature. During this variation, the suitable grain structure with good conductivity is hopefully to achieve.

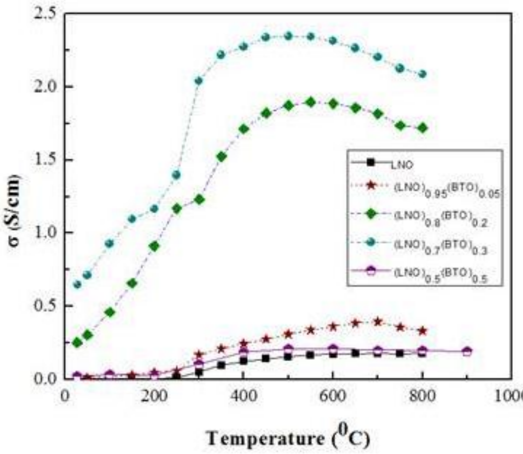

Figure 5. Temperature dependence of electrical conductivity of LNO/BTO composites.

4. CONCLUSIONS

The composite $(LNO)_{1-x}(BTO)_x$ is prepared by chemical method where the components are produced by hydrothermal and sol-gel one. It is shown that these composites have core- shell like grain structure, where core contains nano LNO, BTO crystallites and shell is amorphous. It is evidenced that this special grain structure at suitable component fractions (x=0.3) enhances electrical conductivity up to 20 times comparing with the bare LNO one. The observed advantage stimulates potential to use the LNO/BTO composite for SOFC' cathodes.

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TÓM TẮT

CẤU TRÚC, TÍNH CHẤT ĐIỆN VÀ KHẢ NĂNG ỨNG DỤNG LÀM CA-TỐT CHO PIN NHIÊN LIỆU RẮN CỦA COMPOSITE $(La_2NiO_{4\pm\delta})_{1-x}(BaTiO_3)_x$(x=0.0-0.5)

Lê Thị Anh Thư, Hà Thị Hường[1], Nguyễn Ngọc Đỉnh[1], Huỳnh Đăng Chính[2], Đặng Thị Minh Huệ[2], Makio Kurisu[3], Kensuke Konishi[3], Bạch Thành Công[1]

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Composite $(La_2NiO_{4\pm\delta})_{1-x}(BaTiO_3)_x$ (LNO/BTO), x=0.0, 0.05, 0.2, 0.3, 0.5 được chế tạo và nghiên cứu cấu trúc va tính chất điện. Vật liệu $La_2NiO_{4\pm\delta}$ đơn pha được nung thiêu kết tại 1000 ^oC trong 12 h trong không khí. Độ dẫn điện được đo bằng phương pháp bốn mũi dò trong vùng nhiệt độ cao. Kết quả nghiên cứu cho thấy mẫu x=0.3 có độ dẫn tốt nhất. Cấu trúc lõi vỏ được hình thành giữa BTO và LNO đóng vai trò quan trọng trong sự tăng độ dẫn của vật liệu. Đặc trưng dẫn của vật liệu chuyển từ kim loại sang bán dẫn trong khoảng nhiệt độ 400 đến 700 ^0C. Hệ LNO/BTO có độ dẫn tốt ở vùng nhiệt độ này là thích hợp cho việc chế tạo ca-tốt của pin nhiên liệu rắn.

Keywords: cathode, Solid Oxide Fuel Cells, LNOBTO.