Properties of Cu, Ni, and V doped-LaCrO$_3$ interconnect materials prepared by Pechini, ultrasonic spray pyrolysis and glycine nitrate processes for SOFC

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Abstract The ceramic interconnect, La$_{0.8}$Sr$_{0.05}$Ca$_{0.15}$(Cr$_{1-x}$, B$_x$)O$_3$ (B = Cu, Ni, V, x = 0.02, 0.1, 0.5) (LSCCB) powders were prepared by Pechini method, Ultrasonic Spray Pyrolysis (USP) and Glycine Nitrate Process (GNP). Nano sized powders were synthesized by GNP and their chemical compositions were confirmed by ICP analysis. The electrical conductivities of LSCCCu, LSCCNi, and LSCCV samples were 34 S/cm, 48 S/cm, and 22 S/cm at 800°C in air, respectively. Among the LSCCB powders, the LSCCNi sample shows highest relative density and electrical conductivity. In a low oxygen partial pressure, however, LSCCV sample was more stable. The perovskite phase of the composition LSCCV sample is of large practical interest for interconnects in SOFC because of the stability in low oxygen partial pressure.

Keywords Ceramic interconnect, Pechini method, Ultrasonic spray pyrolysis, Glycine nitrate process, Solid oxide fuel cell

1 Introduction

Solid oxide fuel cell (SOFC) is the most efficient device among the energy technology invented so far for conversion of chemical fuels directly into electrical power. There are two main components of cell and interconnect in SOFC. The interconnect is to connect the anode of one cell to the cathode of the next cell in electrical series. The interconnect materials clearly must have good electrical conductivity and be stable in both oxidizing atmosphere and reducing atmosphere, be close to those of the other cell components in thermal expansion coefficients (TECs), and have low permeability to oxygen and hydrogen [1, 2]. The substitution of either on A or B sites in the ABO$_3$ perovskite materials is currently used to improve electrical properties and sinterability of interconnect materials. Although thermal and electrical properties of the alkaline-earth-doped lanthanum chromites are sufficient for interconnect materials, its sinterability is very low due to the high vapor pressure of the chromium species during the sintering process [3–5].

To increase the performance and durability of the SOFC cells, the ceramic interconnect material with good sinterability and high electrical conductivity is required. Among the alkaline-earth-doped lanthanum chromites, the (La,Ca)CrO$_3$ (LCC) has been used as the ceramic interconnect because it has a good sinterability. However, the LCC has some problem in Ca migration during cosintering on the anode tube. To prevent the Ca migration, the Sr and Ca doped lanthanum chromite (LSCC) was studied in our work [6]. The LSCC has still high sintering temperature although its sintering temperature is lower than that of the LSC. Recently, several attempts have been also made to densify lanthanum chromites with B-site dopants [7–12]. Armstrong et al. [13] is different from the present work in dopant Ca element and preparation method. However, there is still some problem in the sinterability and sintering temperature.

In this work, La$_{0.8}$Sr$_{0.05}$Ca$_{0.15}$(Cr$_{1-x}$,B$_x$)O$_3$ (LSCCB) doped to B site with Copper, Nickel and Vanadium elements

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was investigated to improve the sinterability and the electrical conductivity of the LSCC, and their powders were prepared by Pechini method, Ultrasonic Spray Pyrolysis (USP) and Glycine Nitrate Process (GNP) and their properties were characterized.

2 Experimental

The $La_{0.8}Sr_{0.05}Ca_{0.15}Cr_{0.98}Cu_{0.02}O_3$ (LSCCCu), $La_{0.8}Sr_{0.05}Ca_{0.15}Cr_{0.9}Ni_{0.1}O_3$ (LSCCNi), and $La_{0.8}Sr_{0.05}Ca_{0.15}Cr_{0.95}V_{0.05}O_3$ (LSCCV) were prepared by the Pechini method, Ultrasonic Spray Pyrolysis (USP), and Glycine Nitrate Process (GNP). In Pechini method, the metal nitrates as starting materials were used. Citric acid and ethylene glycol in equivalent molar proportion to the amount of the metal cations were added into the solution of nitrates and the charred resins were calcined at 1000°C for 5 h. The concentration of the nitrates for USP such as LSCCCu, LSCCNi and LSCCV was 0.1 mol/ℓ. The solution was atomized at resonant frequency of 1.7 MHz by an ultrasonic nebulizer. Droplet was conducted to a reactor by the carrier gas of air with a flow rate of 30 ℓ/min and pyrolized at 850°C. These precursors were heat-treated at 1000°C for 5 h. In GNP, glycine content was derived from the total oxidizing and reducing valence of the oxidizer and fuel. The ignition temperature was measured as a function of time.

The as-calcined powder was examined by SEM (HITACHI, S-4700) and XRD (Rigaku, Rint-2000) Cu Kα, 2θ = 20 – 80° and scanning speed of 3°/min. Lattice parameters and structure symmetry of the sintered samples were evaluated by XRD. The BET specific surface areas of the as-calcined powders were measured with the BET analyzer (ASAP2010, Micromeritics Ins. Corp.). The chemical compositions of calcined powders at 1000°C were confirmed by chemical analysis using the ICP-AES. The uncertainty of the element contents in the samples amounted to ±3%. The powders were uniaxially pressed at 70 MPa and sintered at 1400°C and 1500°C for 5 h. The relative densities were estimated by Archimedes method. Electrical conductivity was measured by DC four probe method in air and in various pO_2 at 800°C.

3 Results and discussion

Figure 1 shows the X-ray diffractions of the LSCCB powders synthesized by Pechini method, USP, and GNP. The calcination of powders prepared by Pechini method was carried out at 1000°C for 5 h and the as-calcined powders were a single perovskite phase. The precursors prepared by USP in greenish color were an amorphous phase. Their precursors were not fully decomposed in the heating zone. After calcining at 1000°C for 5 h, their powders showed a single perovskite phase. On the other hand, the precursor powders in GNP were a single perovskite phase because the GNP proceeded by a violent exothermic reaction and completed only within a few seconds. The auto-ignition was observed at approximately 120–130°C and the combustion reaction finished at 600°C or above. The GNP was more effective method to obtain single perovskite phase at lower temperature than those of Pechini method and USP. The lattice parameters of a sintered bulks were a = 5.479Å, c = 13.469Å (LSCCCu), a = 5.472Å, c = 13.472Å (LSCCNi) and a = 5.491Å, c = 13.379Å (LSCCV), respectively. The crystal structures of LSCCB materials were a rhombohedral (hexagonal).

Table 1 shows the chemical compositions of the synthesized powders by ICP analysis. The LSCCCu and LSCCNi powders prepared by Pechini method and GNP were similar to the nominal compositions. Figure 2 shows the SEM image of the as-calcined powders prepared by Pechini method at 1000°C and of the precursors prepared by USP and GNP. Table 2 shows the average particle size and BET specific surface area of the synthesized powders. The average particle sizes (d_{50}) of as-calcined powders by Pechini method were 0.45–0.6 μm and their powders showed a slight agglomeration. The morphology of the precursors prepared by USP was a spherical shape with a various particle-size distribution between submicron and micron size, and their average particle sizes were 1.45–1.65 μm. In GNP, the precursors showed a

Table 1 Chemical compositions of $La_{0.8}Sr_{0.05}Ca_{0.15}Cr_{0.98}Cu_{0.02}O_3$ (LSCCCu), $La_{0.8}Sr_{0.05}Ca_{0.15}Cr_{0.9}Ni_{0.1}O_3$ (LSCCNi), and $La_{0.8}Sr_{0.05}Ca_{0.15}Cr_{0.95}V_{0.05}O_3$ (LSCCV) powders prepared by Pechini method and GNP (ICP-AES)

	Composition					
	LSCCCu (mol%)		LSCCNi (mol%)		LSCCV (mol%)	
Element	Pechini	GNP	Pechini	GNP	Pechini	GNP
La	16.00	15.99	16.04	15.98	16.12	16.13
Sr	1.02	1.02	1.01	1.02	1.03	1.02
Ca	3.06	3.07	3.05	3.06	3.07	3.07
Cr	19.50	19.50	17.91	17.95	18.89	18.88
Cu	0.42	0.42	–	–	–	
Ni	–	–	1.99	1.99	–	–
V	–	–	–	–	0.89	0.90

Fig. 1 X-ray diffraction patterns of the calcined powders and precursors:
(a) $La_{0.8}Sr_{0.05}Ca_{0.15}Cr_{0.98}Cu_{0.02}O_3$,
(b) $La_{0.8}Sr_{0.05}Ca_{0.15}Cr_{0.9}Ni_{0.1}O_3$,
(c) $La_{0.8}Sr_{0.05}Ca_{0.15}Cr_{0.95}V_{0.05}O_3$
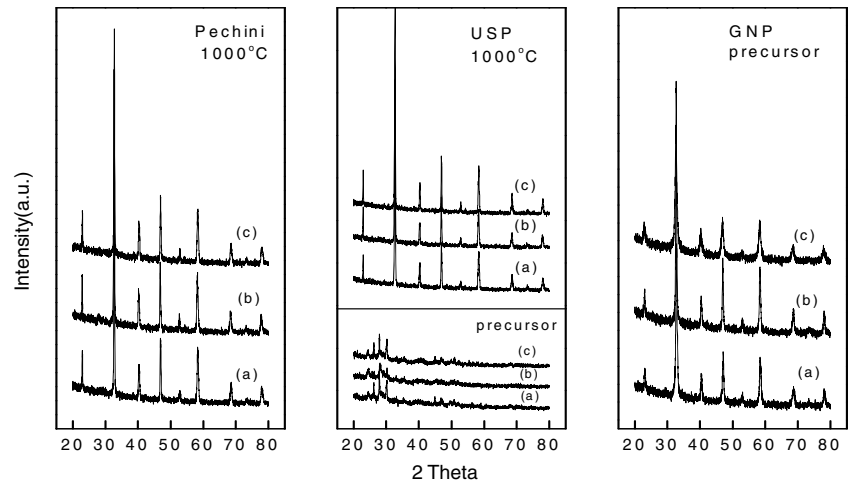
Fig. 2 SEM images of the calcined powders and precursors: LSCCCu: $La_{0.8}Sr_{0.05}Ca_{0.15}Cr_{0.98}Cu_{0.02}O_3$, LSCCNi: $La_{0.8}Sr_{0.05}Ca_{0.15}Cr_{0.9}Ni_{0.1}O_3$, LSCCV: $La_{0.8}Sr_{0.05}Ca_{0.15}Cr_{0.95}V_{0.05}O_3$

porous agglomerated structure due to a sudden evaporation of gas (N_2, CO_2, and H_2O). The primary particle size of LSC-CNi precursor could not be estimated by SEM, because the average particle size was approximately below 10nm. The result of BET specific surface area was a similar to the average particle size in all powders.

Figure 3 shows the relative density of the sintered bulks at 1400°C and 1500°C for 5 h. Generally, an acceptable relative density of the ceramic interconnect have been reported to be

≥94% [14]. The relative densities of LSCCCu and LSCCNi samples prepared by Pechini method and USP were over 94% at 1400°C, but only LSCCV sample prepared by Pechini method at 1500°C was accepted from the viewpoint of the relative density condition. Armstrong et al. [13] reported that their study showed that samples can be fully densified by modifying the chromite compositions with 5 mol% V or 2 mol% Cu. Vanadium has a limited solubility in the LSC lattice and upon sintering it reacts with $SrCrO_4$
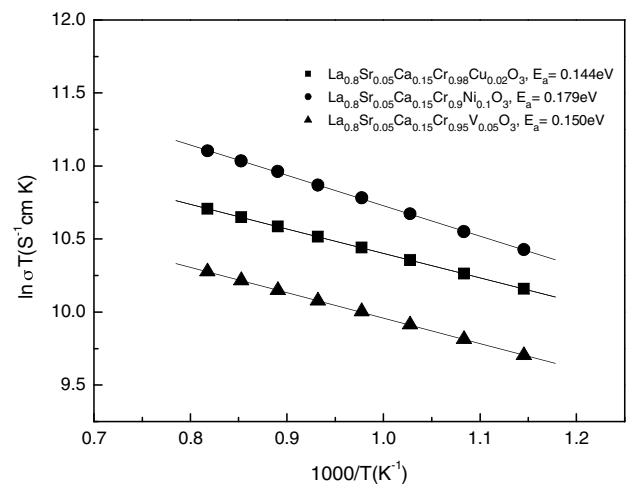
Table 2 The average particle size and BET specific surface area of the synthesized powders

	Analysis					
	Average particle size (μm)			BET specific surface area (m^2/g)		
Composition	Pechini (1000°C, 5 h)	USP (precursor)	GNP (precursor)	Pechini (1000°C, 5 h)	USP (precursor)	GNP (precursor)
LSCCCu	0.52	1.45	<0.01	1.78	0.65	25
LSCCNi	0.45	1.82	–	1.86	0.53	10
LSCCV	0.6	1.65	<0.01	1.70	0.55	39
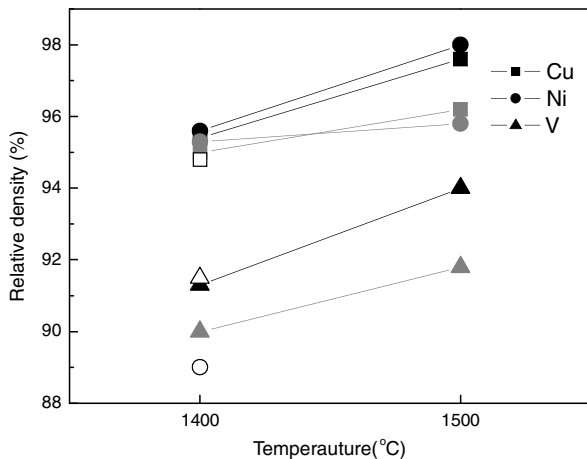
Fig. 3 Relative densities of the $La_{0.8}Sr_{0.05}Ca_{0.15}Cr_{0.98}Cu_{0.02}O_3$, $La_{0.8}Sr_{0.05}Ca_{0.15}Cr_{0.9}Ni_{0.1}O_3$, and $La_{0.8}Sr_{0.05}Ca_{0.15}Cr_{0.95}V_{0.05}O_3$ after sintering at 1400°C and 1500°C for 5 h. (Black color: Pechini method, Gray color: USP, White color: GNP)

Fig. 4 Electrical conductivities and activation energies of $La_{0.8}Sr_{0.05}Ca_{0.15}Cr_{0.98}Cu_{0.02}O_3$, $La_{0.8}Sr_{0.05}Ca_{0.15}Cr_{0.9}Ni_{0.1}O_3$, and $La_{0.8}Sr_{0.05}Ca_{0.15}Cr_{0.95}V_{0.05}O_3$ prepared by Pechini method in air

to form $Sr_3(VO_4)_2$. $Sr_3(VO_4)_2$ liquid phases can readily enhance the sintering behavior of ceramics, however, $Sr_3(VO_4)_2$ phase is reported to melt at 1596°C [15] and Simner et al. [16] reported that $La_{0.85}Sr_{0.15}Cr_{1-x}M_xO_3$, where $0.02 \leq x \leq 0.1$ and M = Co, Cu, Ni and V, typically yielded densities greater than 93% theoretical after sintering at 1450–1550°C for 2 h. In this work, the relative density of LSCCV sample prepared by Pechini method was 94% slightly lower than their results due to Sr content and Cr evaporation as gaseous CrO_3 at high temperature, which disturb the densification of the $LaCrO_3$ particles by vaporization-condensation transport mechanism. Also, $Sr_3(VO_4)_2$ phase of LSCCV sample sintered at 1500°C was not detected. The relative density increased with sintering temperature and doping of Cu or Ni. However, the relative density did not depend on particle size of the precursor powders. Although the particle size of the V-doped samples synthesized by GNP was smaller than that of the samples by USP, the relative density of the Cu-doped samples synthesized by USP was considerably higher than that of GNP. This shows that the dopant is more effective factors for the sinterability of the doped LSCCB materials.

Figure 4 shows the electrical conductivities and activation energies of bulks prepared by Pechini method in air. The

electrical conductivities of LSCCCu, LSCCNi and LSCCV bulks were 34 S/cm, 48 S/cm, and 22 S/cm at 800°C in air, respectively. The electrical conductivity and activation energy of LSCCNi bulk was 34–54 S/cm and $E_a = 0.179$ eV in the range of temperature (600–950°C), and the electrical conductivity of LSCCCu bulk was slightly lower than that of LSCCNi bulk. The relative density increased with the doping of Cu or Ni. This result suggests correlation between relative density and dopant element. The increased relative density enhances conductivity. Armstrong et al. [13] reported that Cu acts as an acceptor in the perovskite lattice, however, the presence of a small amount of Cu provides another undetermined mechanism for enhancing the conductivity. Kononyuk et al. [17] reported Ni doping results in a drastic increase of electronic conductivity and a transition to a metallic conductor typical for $LaNiO_3$, but, the stability and solid solution limit are considerably low. Also, Yasuda et al. [18] reported that the activation energy of $La_{0.8}Sr_{0.2}Cr_{0.95}Ni_{0.05}O_3$ was 0.11eV, which suggests electrical conduction by the small-polaron hopping mechanism.

Figure 5 shows the oxygen partial pressure (pO$_2$) dependence of the electrical conductivities of the sintered bulks prepared by GNP at 800°C. At lower oxygen partial pressure than about 10^{-6} atm, the conductivity decreases drastically with decreasing oxygen partial pressure.
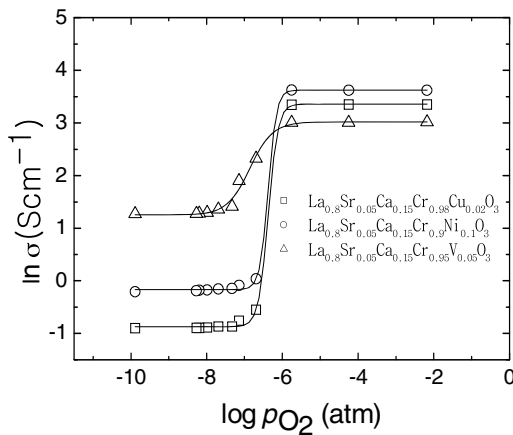
Fig. 5 Electrical conductivities of the sintered bulks prepared by GNP at 800°C in air as a function of pO_2 at 800°C

Although the electrical conductivities of the LSCCCu and LSCCNi bulks were higher than that of the LSCCV sample at higher oxygen partial pressure, the LSCCV bulk was more stable in low oxygen partial pressure. Zuev et al. [19] reported that the acceptor dopant Cu on B-site changes its oxidation state continuously from 3+ via 2+ to 1+ if the oxygen partial pressure decreases. According to Yasuda et al. [18], at low pO_2, the conductivity of $La_{1-x}Sr_xCr_{1-y}Ni_yO_3$ composition was described by the diffusion model with consideration of the effect of surface reaction.

4 Conclusion

The ceramic interconnects of LSCCCu, LSCCNi and LSCCV powders were synthesized by Pechini method, USP, and GNP. The synthesized powders prepared by GNP had a nano particle size (<10 nm), and the calcined powders had a single perovskite phase and a rhombohedral (hexagonal) structure. Also, the chemical composition of the synthesized powder by ICP analysis was almost consistent with a theoretical composition. The relative density increased with sintering temperature and doping of Cu or Ni. This result suggests no correlation between relative density and particle size characteristics. The LSCCCu and LSCCNi bulks prepared by Pechini method and USP showed higher relative densities and electrical conductivities. In low oxygen partial pressure, however, the electrical conductivities of the LSCCCu and LSCCNi bulks decreased drastically. Additionally, the electrical conductivity of LSCCV bulk was more stable than that of LSCCCu and LSCCNi in low oxygen partial pressure. Therefore, the perovskite phase of the composition LSCCV are of large practical interest for interconnects in solid oxide fuel cells because of their more stability in the oxygen partial pressure range.

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