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# Lanthanum based iron and cobalt-containing perovskite using an inorganic nanodispersants aqueous solution

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Nano structured lanthanum based iron and cobalt-containing perovskite has a high potential for a cathode material in intermediate temperature solid oxide fuel cells (IT-SOFCs) (700 - 800 °C) due to its high electro-catalytic activity at a relatively low operating temperature. In this study, nanocrystalline  $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3.5}$  (LSCF) materials are successfully synthesized using a complex method with carbon black (CB) and aqueous dispersion of carbon black (AqCB) as inorganic nanodisperasnts. When AqCB is used as dispersants, the surface areas of LSCF powder increase from 25 m<sup>2</sup>g<sup>-1</sup> to 40 m<sup>2</sup>g<sup>-1</sup>. The cathode sintered at 800 °C of LSCF with CB shows polarizations of 0.10  $\Omega$ cm<sup>2</sup> and 0.28  $\Omega$ cm<sup>2</sup> at 700 °C and 650 °C, respectively. The polarizations of LSCF with AqCB are 0.08  $\Omega$ cm<sup>2</sup> and 0.13  $\Omega$ cm<sup>2</sup> at 700 °C and 650 °C, respectively. The increment in surface area of AqCB-LSCF results in a lower cathode polarization and a higher electro-catalytic activity. The aqueous dispersion of CB is a good candidate as an inorganic dispersant for synthesis of nanocrystalline cathode materials in views of enhanced catalytic activity and lowered contamination.

Key words: Solid oxide fuel cell, La<sub>0.58</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-8</sub>, Nanodispersant, Anode supported cell, Mixed ionic electronic conductor.

### Introduction

Solid oxide fuel cells (SOFCs) are believed to be the most promising candidates for the future energy generation systems for power plants and distributed power. For the state-of-the-art anode-supported SOFC operating at 800 °C, the performance of the conventional  $La_{1x}Sr_{x}MnO_{3-\delta}$  (LSM)-based cathode is not satisfactory due to sluggish oxygen reduction reaction (ORR) kinetics, which causes a low current capacity of the cell [1, 2]. Moreover, most of the electrochemical reactions in LSM-based cathodes using pure electronic conducting materials are restricted to the triple phase boundary of the electronic conducting sites, the ionic conducting sites, and the gaseous oxygen. Hence, considerable efforts are being made to develop a new class of perovskite-based cathode materials for SOFCs that have mixed ionic and electronic conductivity with a high electro-catalytic activity for oxygen reduction at a relatively lower operating temperature (700 - 800 °C) [1-11]. Among these, iron and cobalt-containing perovskites (LSCF) are good candidates for SOFC cathode materials, because of their high electronic and ionic conductivity as well as a high oxygen permeability and electrocatalytic activity. With a Gd-doped ceria (GDC)-based interlayer, the perovskite-based compounds having the general formula  $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$  have been reported to be very effective for intermediated temperature SOFC (700 - 800 °C) applications because of a high catalytic activity of LSCF and suppressing the formation of resistive phase such as strontium zirconate, due to GDC diffusion blocking layer [5, 6, 10-14].

The electrochemical performance of anode-supported SOFCs with a LSCF-type cathode can also be varied by processing and micro-structural parameters of the cathode materials [5, 14]. Small-particle-size and highsurface area in nanocrystalline materials are favored for the cathode electrode for SOFCs [15-17], which results in enhancement of an electro-catalytic reduction of oxidant along with a higher catalytic activity [18-20]. The nanocrystalline cathodes can be easily sintered and the extent of sinterability of these powders can be controlled by the amount of the organic binder added during the preparation of the thick film paste for screen printing. Nevertheless, the high temperatures involved for phase formation of cathode materials hinder the formation of nanostructures [20-22]. In previous work [23], a complex method with ethylene diamine tetra-acetic acid (EDTA) and citric acid as chelants was used to synthesis La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3.8</sub>. Inorganic nanodispersants, carbon black, were used to control the distribution and size of the nanocrystalline LSCF, and the temperature for LSCF phase formation was lowered from 900 °C to

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600 °C. However, the inorganic nanodispersant is nanosized and low- density particles, which can be easily scattered during the process.

In this work, for synthesis of  $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-a}$ , the inorganic nanodispersant is modified as an aqueous solution for being easily controlled. The aqueous dispersant is expected to be beneficial to disperse carbon black and break out agglomeration of carbon black. The effects of aqueous dispersion of carbon black are characterized and compared with solid state carbon black.

## **Experimental**

Lanthanum nitrate, strontium nitrate, cobalt nitrate, and ferric nitrate, all in analytical grades, were used as metal sources. As previous work [23], ethylenediaminetetraacetate (EDTA) powder and crystallized citric acid were used as the raw materials for chelation, which both have purities higher than 99.5%. Lanthanum nitrate  $(La(NO_3)_3)$  $\cdot$  6H<sub>2</sub>O) of 7.54 g (0.017 mol), strontium nitrate (Sr(NO<sub>3</sub>)<sub>2</sub>) of 2.54 g (0.012 mol), cobalt nitrate (Co(NO<sub>3</sub>)<sub>2</sub>  $\cdot$  6H<sub>2</sub>O) of 1.75 g (0.006 mol), and ferric nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>  $\cdot$  9H<sub>2</sub>O) of 9.70 g (0.024 mol) were dissolved in 100 ml of deionized water to prepare a homogeneous metal nitrate solution. The solid citric acid of 11.47 g (0.06 mol) was added to the mixed metal nitrate solution. EDTA powder of 8.77 g (0.03 mol) was introduced and the solution was heated in a water bath at 70 °C. After getting a clear solution, HI BLACK170 (HB170, low color furnace carbon black), which has a surface area of 23 m<sup>2</sup>g<sup>-1</sup> and particle size of 58 nm, was added as an inorganic nano dispersant for CB-LSCF. For AqCB-LSCF, AqCB was added to a metal nitrate precursor solution. AqCB, an aqueous solution of HB170, was prepared with HB170 and 20 wt% of W33 (CHEMNINE<sup>©</sup>, modifier ethoxylated acetylenic diol) aqueous inorganic dispersant by milling with zirconia ball for 24 hrs. The HB170 of 5 g with the form of CB and AqCB was added to a clear solution. LSCF synthesized without CB or AqCB, LSCF, was also prepared. The mixture was reheated to evaporate the water until the magnetic bar stopped rotating. The remaining mixture was dried overnight at 80 - 120 °C in a vacuum oven to remove residual water. The dried powders were crushed and calcined at 500 °C - 900 °C to form a perovskite phase removing the organic compounds and inorganic nanodispersants.

The particle distributions of CB and AqCB were characterized with a particle size analyzer, Delsano. The calcined powders were characterized by X-ray diffractometer and scanning electron microscope (SEM) to observe the phase and the morphologies. Thermogravimetric analysis (TGA, Shimadzu TA-50) was carried out from room temperature to 1000 °C in air at 3 °C min<sup>-1</sup> to investigate the thermal behavior. The specific surface area (SSA) of the powder was calculated by the BET method from the nitrogen adsorption isotherms.

To characterize the cathode polarization, the synthesized powders were mixed with 50 wt% of organic binder solution, ethyl cellulose, di-ethylene glycol butyl ether, and  $\alpha$ -terpinol. For the composite cathode, gadolinium doped ceria (Semi materials, GDC) was mixed with AqCB-LSCF at the weight ratio of 50:50. The cathode paste were screen-printed on both sides of yttrium stabilized zirconia (YSZ) electrolyte, which was prepared by a sintering at 1370 °C for 5 hrs with YSZ tape and the active cathode area is  $0.785 \text{ cm}^2$ . The symmetric cells, which consist of cathode/YSZ/cathode, were sintered at 800 °C and 900 °C. The cathode polarizations were characterized by the impedance measurements. The impedance spectra were obtained in the frequency range of 100 kHz to 0.1 Hz with applied AC voltage amplitude of 100 mV at temperature range of 650 °C to 800 °C.

## **Results and Discussion**

HB170, carbon black (CB), was used as an inorganic nanodispersant for La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> at previous work [23] and the surface area of La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-</sub>  $\delta$  increased, which resulted in the higher fuel cell performances. In this study, HB170 was dispersed in aqueous solution to break the agglomeration of solid HB170 particles, which is expected to increase the surface area of LSCF. To study the effects of the aqueous dispersion of HB170 for La<sub>0.58</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> synthesis, a solid state HB170 (CB) and an aqueous dispersion of HB170 (AqCB) were used. The particle size and distribution of CB and AqCB were characterized using a particle size analyzer and are shown in Fig. 1. CB has 1874 nm of an average particle size and 0.565 of a polydispersity index (PDI). AqCB shows the particle size of 260 nm and 0.174 of PDI. The milling process with an aqueous dispersant is effective to break the agglomeration of CB into smaller particles. AqCB shows the smaller average particle size and the narrower PDI, which is expected to be a more effective to disperse LSCF. Furthermore, HB170 is a nano-sized and lowdensity carbon black, which can easily contaminate the



Fig. 1. Particle size analysis of nanodispersants.



Fig. 2. TGA analysis of LSCF with an aqueous nanodispersant.

environment by diffusing into the air when CB is added into the metal nitrate solution. The aqueous form of HB170, AqCB, can be stored without the spreading of dust, which will be very helpful and eco-friendly for mass production.

The thermal behaviors of the synthesized LSCF mixtures are shown in Fig. 2. The thermal analysis curves were obtained after drying the mixture at 80 -120 °C in a vacuum oven for 12 hrs. Significant weight losses in CB-LSCF are observed at ~175 °C, 300 °C, and 450 °C due to the decomposition of organic compounds, such as citric acid and EDTA, and HB170. AqCB-LSCF has weight losses at ~200 °C, 280 °C, 400 °C, and 500 °C due to the decomposition of organic and inorganic compounds of citric acid, EDTA, WA33, and HB170. The temperatures for weight loss of AqCB-LSCF are shift to lower or higher temperature than those of CB-LSCF, which may results from the interaction among the compounds. All of organic chelants and nano dispersants are decomposed below 600 °C, and the change of weights is not observed above 600 °C. However, the heat flows for the phase formation of LSCF are observed above 600 °C. The perovskite peaks of LSCF, CB-LSCF, AqCB-LSCF appear from 600 °C in the XRD spectra as shown in Fig. 3, which is a relatively lower temperature compared with the temperature over 900 °C by combustion methods or other powder synthesis methods [20-22]. However, the temperature for phase formation is almost identical in all samples, LSCF, CB-LSCF, and AqCB-LSCF.

The SEM images of calcined powder are shown in Figs. 4 and 5. The size of CB-LSCF and AqCB-LSCF calcined at 600 °C and 700 °C is less than 60 nm and the agglomerated particles of CB-LSCF and AqCB-LSCF are easily observed in the morphologies calcined at 800 °C and 900 °C. The particles in AqCB-LSCF are slightly better dispersed and smaller than those in CB-LSCF. The change of particle size and distribution are unclear by SEM images. However, BET measurement shows the increment of the surface area of AqCB-LSCF. The surface areas of the CB-LSCF are 25 m<sup>2</sup>g<sup>-1</sup> and 14 m<sup>2</sup>g<sup>-1</sup> calcined at 600 °C and 700 °C, respectively.



**Fig. 3.** XRD pattern from (a) LSCF, (b) CB-LSCF, and (c) AqCB-LSCF.



Fig. 4. SEM images of CB-LSCF with calcined at 600 °C-900 °C.



**Fig. 5.** SEM images of AqCB-LSCF with calcined at 600 °C-900 °C.



Fig. 6. Impedance Spectra of symmetric cell sintered at 800 °C.

The surface areas of AqCB-LSCF are  $40 \text{ m}^2\text{g}^{-1}$  and  $24 \text{ m}^2\text{g}^{-1}$  calcined at 600 ° and 700 °, respectively. The addition of AqCB results in the increase in surface areas, which is expected to have the higher electrocatalytic activities.

To characterize the cathode performances with impedance spectra, the symmetric cells with YSZ electrolyte of -230  $\mu$ m were fabricated with LSCF, CB-LSCF, and AqCB-LSCF, which are calcined at 700 °C. AqCB-LSCF and gadolinium doped ceria composite cathode was also fabricated for the impedance analysis. The cathode materials were screen-printed three times for adjusting the cathode thickness of -20  $\mu$ m. The symmetric cells were sintered at 800 °C and 900 °C to investigate the effects of the sintering temperature on the impedance spectra. Figs. 6 and 7 show the impedance spectra of symmetric cells with LSCF, CB-LSCF, AqCB-LSCF, and composite cathode (Aq-LSCF and GDC) sintered at 800 °C and 900 °C.

Impedance spectra of symmetric cells represent the ohmic resistance and the cathode polarization. The ohmic resistance includes the resistance of electrolyte, the resistance of electrode, and the interfacial resistance between electrolyte and electrode. Here, the conductivity of electrolyte is same in all case. The difference in



Fig. 7. Impedance Spectra of symmetric cell sintered at 900 °C.

Table 1. The cathode polarization with temperature of LSCFs in symmetric cells sintered at (a) 900  $^{\circ}$ C and (b) 800  $^{\circ}$ C (a)

			(u)	
Polarization (Ωcm <sup>2</sup> ) of cathodes sintered at 900 °C				
	LSCF	CB-LSCF	AqCB-LSCF	AqCB-LSCF & GDC
800 °C	0.02	0.02	0.02	0.02
750 °C	0.06	0.05	0.05	0.04
700 °C	0.17	0.17	0.15	0.10
650 °C	0.53	0.52	0.49	0.27
(b)				
Polarization ( $\Omega$ cm <sup>2</sup> ) of cathodes sintered at 800 °C				
	LSCF	CB-LSCF	AqCB-LSCF	AqCB-LSCF & GDC
800 °C	0.02	0.02	0.01	0.01
750 °C	0.04	0.03	0.03	0.02
700 °C	0.11	0.10	0.08	0.05
650 °C	0.32	0.28	0.13	0.15

ohmic resistances is from the interfacial resistance between cathode and electrolyte. AqCB-LSCF cathode shows the lowest value of ohmic resistance at all temperature. The higher surface areas of AqCB-LSCF can be easily sintered, and formed the interface effectively with YSZ electrolyte, which results in the lowest ohmic resistance. However, the composite of AqCB-LSCF and GDC shows the higher ohmic resistance, which results from the hindrance of GDC for formation of interface with YSZ. The cathodes sintered at 800 °C have the lower ohmic resistance than those sintered at 900 °C, which means that the interfacial resistance at 800 °C is lower than that at 900 °C. With the impedance spectra of symmetric cells, the cathode polarizations are obtained by dividing with two of the difference between the intercept polarization at low frequency and high frequency. With increasing temperature, the decreases of the polarizations are observed. The results of cathode polarization are



Fig. 8. Images of AqCB-LSCF at sintering temperature of 800 and 900  $^{\rm o}{\rm C}.$ 

summarized in Table 1. The cathode polarization decreases by using CB and AqCB as an inorganic dispersants, when compared with LSCF. The polarizations of the cathodes show the similar values at higher temperature (750 °C and 800 °C). However, with decreasing temperature, the effects of high surface area are dominant and the AqCB-LSCF shows the lower polarization than LSCF and CB-LSCF. Furthermore, the cathode performance can be enhanced using GDC for increasing the ionic conductivity and hindering cathode sintering [24], which results in the lowered polarization in composite cathode. The cathodes sintered at 900 °C have the higher cathode polarization than those sintered at 800 °C. The cathode polarization depends on the surface area of cathode materials, which can be controlled by sintering temperature. The sintering process at higher temperature increases the resistance due to particle agglomeration and lower active area. As shown in Fig. 8, the cathode sintered at 900 °C has more agglomeration and larger particle than that at 800 °C. The sintered particles are easily observed in the cathode sintered at 900 °C, which results in the higher cathode polarization.

## Conclusion

cathode materials Nanocrystalline based on  $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$  are successfully synthesized by a complex method with carbon black (CB-LSCF) and aqueous dispersion of carbon black (AqCB-LSCF). The phase formation for perovskite starts from 600 °C, which is a relatively lower temperature. The surface area of the AqCB-LSCF is 40 m<sup>2</sup>g<sup>-1</sup> from 25 m<sup>2</sup>g<sup>-1</sup> of CB-LSCF. The aqueous dispersion of CB is very beneficial for controlling the particle size of LSCF and a good candidate as a inorganic dispersant to synthesis nanocrystalline cathode materials in a view of contamination. The enhanced cathode performances are more dominant in lower temperature (650 and 700 °C) than higer temperature (750 and 800 °C). The cathode sintered at 800 °C of CB-LSCF shows polarizations of  $0.10 \ \Omega cm^2$  and  $0.28 \ \Omega cm^2$  at 700 °C and 650 °C, respectively. The polarizations of AqCB-LSCF are  $0.08 \ \Omega cm^2$  and  $0.13 \ \Omega cm^2$  at 700 °C and 650 °C, respectively. The sintering temperature also affects the ohmic resistance and cathode polarization. The cathodes sintered at 800 °C show the lower cathode polarization than those at 900 °C. The increment in surface area of AqCB-LSCF results in a lower cathode polarization and a higher electro-catalytic activity.

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