

# Electrical conductivity of cobalt doped $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$

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## Abstract

$\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$  (LSGM8282),  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.15}\text{Co}_{0.05}\text{O}_{3-\delta}$  (LSGMC5) and  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.115}\text{Co}_{0.085}\text{O}_{3-\delta}$  (LSGMC8.5) were prepared using a conventional solid-state reaction. Electrical conductivities and electronic conductivities of the samples were measured using four-probe impedance spectrometry, four-probe dc polarization and Hebb–Wagner polarization within the temperature range of 973–1173 K. The electrical conductivities in LSGMC5 and LSGMC8.5 increased with decreasing oxygen partial pressures especially in the high ( $>10^{-5}$  atm) and low oxygen partial pressure regions ( $<10^{-15}$  atm). However, the electrical conductivity in LSGM8282 had no dependency on the oxygen partial pressure. At temperatures higher than 1073 K,  $P_{\text{O}_2}$  dependencies of the free electron conductivities in LSGM8282, LSGMC5 and LSGMC8.5 were about  $-1/4$ , and  $P_{\text{O}_2}$  dependencies of the electron hole conductivities were about 0.25, 0.12 and 0.07, respectively. Oxygen ion conductivities in LSGMC5 and LSGMC8.5 increased with decreasing oxygen partial pressures especially in the high and low oxygen partial pressure regions, which was due to the increase in the concentration of oxygen vacancies. The change in the concentration of oxygen vacancies and the valence of cobalt with oxygen partial pressure were determined using a thermo-gravimetric technique. Both the electronic conductivity and oxygen ion conductivity in cobalt doped lanthanum gallate samples increased with increasing concentration of cobalt, suggesting that the concentration of cobalt should be optimized carefully to maintain a high electrical conductivity and close to 1 oxygen ion transference number.

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**Keywords:** Electrical conductivity; Hebb–Wagner polarization; Oxygen ion conductivity; Oxygen vacancy; Lanthanum gallate

## 1. Introduction

Oxygen ion conductors with high electrical conductivity are important candidates for electrolytes in solid oxide fuel cells (SOFCs) [1–8]. Cobalt doped  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$  (LSGM8282) perovskites show superior oxygen ion conductivity and good chemical stability [3,6–8], and are regarded as promising candidates for the electrolyte of intermediate temperature solid oxide fuel cells (ITSOFCs).

Efficiency of SOFCs is closely related to the electronic conductivity of the electrolyte, since the minor charge carriers in the electrolyte, i.e., free electrons and electron holes, could lead to a short circuit current [2,9]. The studies of the conductivity of LSGM8282 with a low concentration of cobalt ( $<8.5$  mol%) are still very limited [6–8]. Ishihara et al. [7] investigated the electronic conductivity in cobalt doped LSGM8282 with the ion blocking method. Electronic conductivities at various tem-

peratures in  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.15}\text{Co}_{0.05}\text{O}_{3-\delta}$  (LSGMC5) and electronic conductivities at 1073 K in LSGM8282 doped with various amount of cobalt were reported. It was considered that the extrinsic free electron and electron hole conductivity caused by the redox reactions involving doped cobalt became dominant with decreasing temperatures [8].

Despite the limitations in the number of studies of the conductivity of lanthanum gallate, there are obvious discrepancies among the results reported [6–8,10]. The accuracy of the Hebb–Wagner polarization measurement depends strongly on the operational conditions. It is essential to maintain good sealing of the blocking electrode compartment. Further, special care should be taken to prevent the diffusion of oxygen from the reversible electrode compartment to the blocking electrode compartment [7]. It would be helpful to verify the operating systems by checking some well-studied samples.

The properties of the electrolyte have a strong effect on the polarization resistance of the electrode supported on the electrolyte beside the dominant effect on the ohmic resistance of the cell [11,12]. The cells based on cobalt doped lanthanum gallate exhibited a superior low ohmic resistance and electrode

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polarization resistance compared with the cells supported on  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ .  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.115}\text{Co}_{0.085}\text{O}_{3-\delta}$  exhibited the highest performance among the cobalt doped LSGM8282 electrolytes [12]. It was assumed that the properties of the charge carriers in the electrolyte could play a major role in determining the cell performance. The study of the defects in cobalt doped lanthanum gallate is an important topic, which is closely related to the conductivity of the materials. The decrease in the valence of Co and the increase in the concentration of oxygen vacancies with decreasing oxygen partial pressures of Co doped lanthanum gallate have been characterized using redox titration [8], and a significant oxygen partial pressure dependency of the concentration of oxygen vacancies was observed. However, no effect of oxygen partial pressure on the oxygen ion conductivity in cobalt doped LSGM8282 was reported. This is quite questionable considering that the oxygen ion conductivity should be closely related to the concentration of oxygen vacancies. It would be interesting to further study the electrical conductivity and defect equilibrium in cobalt doped lanthanum gallate in detail.

In this study, three typical lanthanum gallate electrolytes, i.e., LSGM8282, LSGMC5 and LSGMC8.5, were prepared using the conventional solid-state reaction. Electrical conductivities and electronic conductivities of the samples were measured using four-probe impedance spectrometry, four-probe dc polarization and Hebb–Wagner polarization within the temperature range of 973–1173 K. The re-examination of LSGM8282, which is a well-studied material, was to verify the experimental conditions. The change in the concentration of oxygen vacancies and the valence of cobalt with decreasing oxygen partial pressures were determined using thermo-gravimetric technique.

## 2. Experimental

$\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$  (LSGM8282),  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.15}\text{Co}_{0.05}\text{O}_{3-\delta}$  (LSGMC5) and  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.115}\text{Co}_{0.085}\text{O}_{3-\delta}$  (LSGMC8.5) were prepared using the conventional solid-state reaction. The precursors of the samples were  $\text{La}_2\text{O}_3$  (99.99%),  $\text{SrCO}_3$  (99.5%),  $\text{MgO}$  (99.5%),  $\text{Ga}_2\text{O}_3$  (99.99%) and  $\text{CoO}$  (99.99%). Powders of the precursors in stoichiometric ratio were ball-milled for 24 h. The mixture was then pre-calcined at 1273 K for 6 h, after which the pre-calcined mixture was iso-statically pressed into a disk at 274.6 MPa for 10 min. The diameter of the green disk was 2.0 cm. The disks were then sintered at 1773 K for 6 h in air. The sintered disks were polished to a thickness of 1 mm. The phase compositions of the materials were identified using XRD (Panalytical X'pert).

The densities of the sintered disks were measured using the Archimedes technique, and the densities of LSGM8282, LSGMC5 and LSGMC8.5 were 6.39, 6.53 and 6.59 g cm<sup>-3</sup>, respectively, showing relative densities higher than 98%.

The sintered disks were cut into a rectangular shape for electrical conductivity measurements. The dimension of the samples was typically 2 mm × 1 mm × 15 mm. Platinum paste was applied to both end of the bar and calcined at 1173 K for 30 min as working and counter electrode. Two platinum wires were attached to the bar close to the working and counter elec-

trode, respectively, as two reference electrodes. The electrical conductivities were measured as a function of temperature in a mixture of N<sub>2</sub> (99.99%) and water saturated H<sub>2</sub> (99.99%), or oxygen (99.99%) and N<sub>2</sub> (99.99%) by using a VMP2/Z-40 electrochemical testing station (AMETECH). The oxygen partial pressure was determined using a zirconia oxygen sensor. The flow rate of the gas mixture was about 100 ml min<sup>-1</sup>. The electrical conductivities were measured by using both the four-probe impedance spectrometry and four-probe dc polarization, the results of which agreed with each other well.

Electronic conductivity was measured using the Hebb–Wagner polarization method [13–15]. Ion-blocking polarization cells of the configuration.

Dense Al<sub>2</sub>O<sub>3</sub> plate, Pt (blocking electrode)/sample/Pt (reversible electrode), air were constructed [7–8,10]. Pt paste was painted on both faces of the samples symmetrically with a diameter about 10 mm and sintered at 1173 K for 30 min. The blank surface of the sample was covered with powders of Pyrex glass to prevent the diffusion of oxygen from the reversible electrode compartment to the blocking electrode compartment. Pyrex glass powder as well as Pyrex glass ring was used for the sealing between the dense alumina plate and the sample, and between the sample and an alumina tube. The mixture of high purity (99.99%) N<sub>2</sub> and O<sub>2</sub> with an oxygen partial pressure about 0.21 atm was used as the reference gas passing over the reversible electrode. The feeding rate of the gas was about 100 ml min<sup>-1</sup>. A constant dc voltage was applied on the sample by using a VMP2/Z-40 electrochemical testing station (AMETECH), and the residual current was measured using the same equipment.

The weight losses in nitrogen of LSGM8282, LSGMC5 and LSGMC8.5 were measured using thermo-gravimetric analyses technique (Netzsh STA409) as a function of temperature. The samples were prepared as follows. Powders of the samples were sintered at 1773 K for 6 h, and then ground into fine powders. Before the measurements, the powders were calcined in air or oxygen for 2 h at 1073 K and then quenched to room temperature quickly. Six samples were tested, which were abbreviated as LSGM8282-air, LSGM8282-oxygen, LSGMC5-air, LSGMC5-oxygen, LSGMC8.5-air and LSGMC8.5-oxygen. The weight losses of the samples were measured in 50 ml min<sup>-1</sup> flowing high purity nitrogen. Oxygen partial pressure of the high purity nitrogen was about 1 × 10<sup>-5</sup> atm as determined by the zirconium oxygen sensor. Three heating rates were tested, i.e., 10, 5 and 2 K min<sup>-1</sup>. The weight loss measured using a heating rate of 5 K min<sup>-1</sup> was the same as that of 2 K min<sup>-1</sup>, which exhibited a relative error within 1–2% compared with that using a heating rate of 10 K min<sup>-1</sup>. Therefore, the weight losses under a heating rate of 5 K min<sup>-1</sup> were reported in this study.

## 3. Results

### 3.1. Phase composition

The XRD patterns of LSGM8282, LSGMC5 and LSGMC8.5 are shown in Fig. 1. The results show that the samples exhibit the same single phase resembling that of  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.87}$ .

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