SYNTHESIS OF $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ BY IMPROVED CITRIC ACID ROUTINE AND CHARACTERIZATION OF ITS PROPERTIES OF ELECTRICAL CONDUCTIVITIES

Jingwang Yan, Yonglai Dong, Chunying Yu and Yi Jiang
Dalian Institute of Chemical Physics
Chinese Academy of Sciences
Dalian 116023, CHINA

ABSTRACT

Solid oxide electrolyte with perovskite structure, $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ (LSGM), was synthesized at relatively low temperatures by improved citric acid routine, i.e. EDTA-citric acid combined complexation method. EDTA was added to the mixed solution of relevant nitrates as a complexant and citric acid as an aid complexing and gelatification agent. The precursors were analyzed by thermogravimetric and differential thermal analyses. X-ray diffractometry (XRD) and infrared spectroscopy (IR) were used to characterize the sintering processes. The morphologies of the powder products were observed by scanning electron microscopy (SEM). NH$_4$NO$_3$ added to the mixed solution had an effect on the initial temperature of crystallization and the granular distribution of the electrolyte powder with pure perovskite structure. Adding NH$_4$NO$_3$ into the mixed solution could further decrease the synthesizing temperature of LSGM and the average particle size of the resultant product. Compared with solid-state reaction method, the synthesizing temperature of LSGM was lowered from 1500°C to 1120°C and much finer products could be obtained. Electrical conductivities of the dense samples derived from LSGM powder synthesized by this new method were investigated at different temperatures and different oxygen partial pressures by a. c. impedance technique.

INTRODUCTION

Solid oxide fuel cells (SOFC) directly convert chemical energy of fuels into electricity without the limitation of Carnot's law. They boast with high energy conversion efficiency, low environmental pollution, etc. Compared with other types of fuel cells, SOFCs have many special advantages: they do not need to use noble metals as electrode catalysts; many fuels, such as natural gas, CO, etc. can be used without pre-treatment; they can be easily combined with turbine to increase the total energy utilization efficiency (1,2,3).

SOFCs operating above 900°C have been widely studied (4). Too high operating temperatures will bring many material problems such as electrode sintering and interfacial reactions between electrodes and electrolyte. One feasible way to overcome these problems is to decrease the operating temperature of SOFCs (1). There are two commonly adopted methods to lower the SOFC operating temperature. One way is fabricating a thin Yttria Stabilized Zirconia (YSZ) film supported on an anode or cathode...
substrate to decrease the internal resistance drop of a SOFC single cell. Another way is using another solid oxide as alternative electrolyte in a SOFC instead of YSZ (5,6).

La$_{1-x}$Sr$_x$Ga$_{1-y}$Mg$_y$O$_{3-8}$ (LSGM) with perovskite structure was firstly synthesized as a new electrolyte by Tatsumi Ishihara in 1994 (7). It is a promising material for intermediate temperature solid oxide fuel cells due to its high ionic conductivity and high oxygen ionic transference number (7,8,9).

There are several methods that can be used to synthesize perovskite-type composite oxides. Solid-state reaction and coprecipitation techniques are often used. A drawback for these methods is the lack of homogeneity, leading to an incomplete reaction of the precursor. New methods have been developed such as hetero-nuclear complex thermal decomposition techniques and sol-gel techniques (10,11,12). Recently pyrolysis of salt cellulose composites has won acceptance in the preparation of solid electrolyte powder such as YSZ (13).

In order to synthesize uniform and ultrafine LSGM powder that can be used for the preparation of supported LSGM films, it is necessary to lower its minimum synthesizing temperature. In this paper, an improved citric acid method, i.e. EDTA-citric acid combined complexation method was introduced for the low temperature synthesis of ultra-fine LSGM powder. TG-DTA, XRD and IR were used to characterize the precursors and the products calcined at different temperatures. Electrical conductivity behavior of LSGM dense disks prepared from the LSGM ultra-fine powder was also examined.

**EXPERIMENTAL**

**Preparation of LSGM Precursor by Improved Citric Acid Method**

Solid oxide electrolyte with perovskite structure, La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_{3-8}$ (LSGM), was synthesized by improved citric acid routine, i.e. EDTA-citric acid combined complexation method. The preparation procedure is presented in Fig. 1. Metal nitrates La(NO$_3$)$_3$·6H$_2$O, Sr(NO$_3$)$_2$ and Mg(NO$_3$)$_2$·6H$_2$O were dissolved in deionized water, and Ga$_2$O$_3$ was dissolved in hot nitric acid to form a clear solution. Their precise concentrations were determined by EDTA titration. These nitrate solutions were mixed in a large beaker and then the EDTA-NH$_3$·H$_2$O solution was added while heating and stirring. Some amount of citric acid was then added, using NH$_3$·H$_2$O to adjust the pH of the system to be around 7. The mole ratio of EDTA acid: citric acid: total metal ions was around 1.2:1.2:1. This solution was separated into two parts. As a contrast experiment, some amount of NH$_4$NO$_3$ (the mole ratio of NH$_4$NO$_3$: total metal ions was about 1:1) was added into one part of this solution and continued heating and stirring on a hot plate until a dark purple gel was formed. For another part of this solution, no NH$_4$NO$_3$ was added and a gel was prepared with the same method. The gels were heated to burn in ceramic containers on an electric heater to form solid precursors.

**Characterization of LSGM Precursor Prepared by Improved Citric Acid Method**

The precursors were sintered at various temperatures for 180 min. X-ray Diffractometer (XRD), Infrared Spectroscopy (IR), Thermogravimetric and Thermal Differential Analysis (TG-DTA) were used for the investigation of the compositive and structural changes of the resultant products during the sintering process. The XRD
patterns were collected on a model D-MAX-RB Powder X-Ray Diffractometer using Cu Ka radiation. IR spectra of those calcined products were performed on a Nicolet Impact 410 FT-IR spectrometer. TG-DTA analyses were performed on a Shimadzu DT-30 Thermal Analyzer and Thermogravimetric instrument.

**Preparation and characterization of LSGM by Solid State Reaction Method**

As a contrast experiment, LSGM was synthesized by a traditional solid-state reaction method. The precursor was prepared by mixing La2O3, SrCO3, Ga2O3 and MgO thoroughly with a pestle and mortar. The precursor was characterized using TG-DTA technique. After the precursor being sintering at various temperatures for 180 min, the resultant products were examined using XRD.

**Measurements of the Electrical Conductivity of LSGM Prepared by Improved Citric Acid Method**

The precursors were thoroughly pulverized and then pre-sintered at 1000°C for 2 h. The pre-sintered precursors were pressed into disks under an axial pressure of 17.76 MPa. These disks were calcined at 1450°C for 360 min and then cut into long bars for the measurement of electrical conductivities. A. c. impedance technique was used to measure the electrical conductivities of LSGM under various temperatures (from 500°C to 900°C) and oxygen partial pressures (from 8.23×10−16 to 1.03 atm). The a. c. impedance spectroscopy collected in the frequency range from 1 Hz to 50 kHz was analyzed using Z-View (Version 2.0b) software. The a. c. impedance system consisted of a Potentiostat/Galvanostat (EG&G Model 173 with Current Converter Model 376), a Lock-in Amplifier (EG&G Model 5204) and a Function Generator (Good Will Instrument Corporation Limited, Model GFG-8109G).

**RESULTS AND DISCUSSION**

**Formation Process of LSGM Prepared by the Improved Citric Acid Method Without Addition of NH4NO3**

Fig. 2 shows the TG, DTG and DTA curves of the LSGM precursor prepared by the improved citric acid method without addition of NH4NO3. The TG and DTA curves were collected at a heating rate of 20 K/min in air with a flow rate of 10 ml/min, and the DTA curve was collected at 10 K/min in still air. Weight loss took place mainly at 390°C to 512°C and it was completed at 820°C. In accordance with this weight loss, there was a large exothermic peak at 390°C to 590°C on the DTA curve, which was attributed to the burnout of the nitrates, complexed EDTA and other organic agents. On the DTA curve, there were other two broad exothermic peaks at 733°C to 950°C and 950°C to 1220°C. For the first broad peak, there was a counterpart on the DTG curve and a weight loss on the TG curve, which corresponded to the decomposition of carbonates formed during the sintering process at lower temperatures and the re-crystallization of the metal oxides. But the second broad peak had no counterpart on the TG and DTG curves. So this exothermic event might associate with a phase transformation process, which was thought to be the formation of LSGM with perovskite structure. From the DTA curve, we can see that the formation of perovskite of LSGM started at 950°C and completed at 1220°C.
Infrared absorption spectra of the resultant products prepared by sintering the precursors at various temperatures for 180 min are shown in Fig. 3. The sintering temperatures for sample 1 to 8 are 290°C, 390°C, 590°C, 740°C, 950°C, 1120°C, 1320°C, and 1450°C respectively. In Fig. 3, the peak at about 1480 cm\(^{-1}\) is assigned to the C-O stretching vibrations of ionized carboxylate, the 1387 cm\(^{-1}\) and 857 cm\(^{-1}\) peaks to ionized nitrates. For the sample, which was sintered at 290°C for 180 min, the organic compounds were almost completely removed and no C-H vibrating absorptions could be observed, but the absorption of ionized carboxylate and nitrates still remained. With the rise of the sintering temperature, the intensity of these peaks became weak. When the sample was sintered at 950°C for 180 min, the peaks associated with NO\(^3\) and CO\(^3\) became very small. The absorption peaks at 1083 cm\(^{-1}\), 1209 cm\(^{-1}\), 1368 cm\(^{-1}\) and 1461 cm\(^{-1}\) were left after the sample being treated at 1120°C for 180 min, and peaks at 903.87 cm\(^{-1}\), 1116 cm\(^{-1}\) and 1375 cm\(^{-1}\) were left after the sample being treated at 1350°C for 180 min.

XRD spectroscopy curves of these samples are shown in Fig. 4. The precursors, which were sintered at 290°C, 390°C, and 590°C respectively, kept amorphous states and no characteristic diffraction peaks could be observed on their XRD patterns. For samples treated at 740°C, several peaks appeared which could be associated with the formation of carbonates and the re-crystallization of some metal oxides. At this temperature, diffraction peaks of perovskite structure began to appear but their intensities were very weak. With the rising of the treating temperatures, the intensities of the characteristic peaks of the perovskite structure were getting stronger and stronger. Till to 1120°C, LSGM powder with perovskite structure was nearly completely formed and there were only some very weak diffraction peaks of other impurity phases left. Above 1120°C, the pure perovskite structure of LSGM was formed after the precursor being treated for 180 min. When we increased the sintering time to 360 min, a pure perovskite structure of LSGM was fully formed at 1120°C. The LSGM powder prepared by this method at 1120°C showed a dark brown color and serious soft agglomeration was observed for this powder. The morphology and particle size of LSGM prepared by this method was observed using Transmission Electron Microscope (TEM). Most particles had irregular forms with radius between 0.6-1.5 μm.

**Formation Process of LSGM Prepared by a Solid State Reaction Method**

Fig. 5 shows the TG-DTA analysis results of LSGM precursor prepared by thoroughly mixing La\(_2\)O\(_3\), SrCO\(_3\), Ga\(_2\)O\(_3\) and MgO with the aid of ethanol. The TG and DTA curves were collected at a heating rate of 10 K/min in air with a flow rate of 10 ml/min, and the DTA curve was collected at 10 K/min in still air. For this sample, loss weight mainly took place at 250°C to 330°C, 650°C to 735°C and 830°C to 900°C. For the weight loss at 250°C to 330°C, there was an endothermic peak on the DTA curve, which was assigned to the decomposition of some organic compositions. These impurities were introduced into the precursor by ethanol which was used as pulverizing aid. The loss weights at high temperatures could be associated with the decomposition of SrCO\(_3\). On the DTA curve, there was a wide exothermic peak starting at 860°C and ending at 1350°C, which could be associated with the reaction between some oxides. Above 1350°C, there emerged another exothermic peak which maybe related with the formation of the perovskite structure of LSGM because no counterpart for this peak could be observed on the TG curve. XRD curves of the resultant products treated at various temperatures for 180 min were shown in Fig. 6. From the XRD analyzing results, we could learn that the
perovskite structure of LSGM began to form at 1320°C. Pure perovskite structure was not formed although the precursor was heated at 1450°C for 180 min. In fact, the precursor should be sintered at 1500°C for about 360 min to get LSGM powder with a pure perovskite structure and at this temperature dense ceramic was formed. These hard glomerates need to be re-pulverized with the aid of ethanol. Because the LSGM powder prepared using this method had very low specific surface area and relatively large average particle size, it was not suitable for the fabrication of supported LSGM films.

Compared with the solid-state reaction method, the minimum synthesizing temperature of LSGM with a perovskite structure could be decreased from 1500°C to 1120°C by introducing the improved citric acid method mentioned above.

**Effects of the Addition of NH₄NO₃ into the Mixed Solution on the Formation Process of LSGM**

The addition of NH₄NO₃ into the mixed nitrate solution had a great influence upon the formation process of the LSGM from the precursor. When the gel with the addition of NH₄NO₃ was heated on an electric heater, it became more and more viscous. Before it began to burn, NH₄NO₃ decomposed dramatically and the released NH₃, NOₓ etc. caused a rapid volume expansion. A very puffed black ash was obtained after the burning. Another character of this process was that the hot viscous gel spilled over the container while burning. This black precursor was extremely fine and light.

When the gel without the addition of NH₄NO₃ was heated, it turned to red after some smoke emitted. When cooling down to the ambient temperature, a white precursor was acquired. The dispersion degree of that precursor was much lower than that of the precursor prepared from the gel with the addition of NH₄NO₃.

Fig. 7 shows the TG-DTA curves of the LSGM precursor prepared from the gel with the addition of NH₄NO₃. The shape of this TG and DTG curve was similar to that the precursor prepared from the gel without the addition of NH₄NO₃. There were some differences between the DTA curves of these two kinds of precursors. On the DTA curve of this precursor, there was only one broad exothermic peak, which was thought to be the combination of two peaks associated with the re-crystallization of the metal oxides and the formation of the perovskite structure of LSGM. This combination of these two peaks was caused by the shift of the high temperature exothermic peak, i.e., the decrease of the formation temperature of LSGM. So from this gel, ultra-fine LSGM could be acquired at a much lower temperature. Fig. 8 shows the particle morphologies of the LSGM powders prepared from the gel with the addition of NH₄NO₃ by TEM. In Fig. 8 (a), the LSGM prepared by sintering the precursor at 1200°C for 180 min is presented and in Fig. 8 (b) the LSGM prepared by sintering the precursor at 1300°C for 180 min is shown. From these TEM pictures we can learn that with the rise of treating temperatures, the particle sizes increased rapidly. The particle sizes of the LSGM powder acquired by sintering the gel at 1200°C were among 20 to 50 nm and the particle sizes of the LSGM powder acquired by sintering the gel at 1300°C increased to 50 to 100 nm. In short, the addition of NH₄NO₃ into the mixed nitrate solution before the gel was formed had great influences on the formation process and granular distribution of resultant LSGM powder.

**Electrical Conductivity of LSGM Prepared by Improved Citric Acid Method**

The temperature dependence of the electrical conductivity (in air) of LSGM prepared by this improved citric acid method with the addition of NH₄NO₃ is present in Fig. 9 and
the relation between its electrical conductivity (at 800°C) and the oxygen partial pressure
was shown in Fig. 10.

Fig. 9 shows that at relatively high temperatures, $\ln(\sigma T)$ changed linearly with $1000/T$, which was in accordance with the Arrhenius equation,

$$\sigma = \frac{\sigma_0 \exp(-\frac{E_a}{RT})}{T}$$

(1)

Where, $\sigma$ is the electrical conductivity of a sample, $E_a$ activation energy of the electrical conductivity, $R$ gas constant, $T$ absolute temperature and $\sigma_0$ a constant. This equation can be rearranged to another form,

$$\ln(\sigma T) = \ln\sigma_0 - \frac{E_a}{RT}$$

(2)

From Equation (2), we can learn that $\ln(\sigma T)$ and $1/T$ have a linear relation. The slope of this line is $-E_a/R$. From this relation, we can easily calculate the activation energy $E_a$ of the electrical conductivity for the samples we investigated. $E_a$ of LSGM prepared by this improved method with the addition of $\text{NH}_4\text{NO}_3$ was 87.21 kJ/mol at high temperature (from 500°C to 900°C).

From Fig. 10 we can see that among a wide range of oxygen partial pressures, the electrical conductivity of LSGM prepared by the improved citric acid method with the addition of $\text{NH}_4\text{NO}_3$ nearly kept constant, which indicated that the LSGM we synthesized was neither a p-type nor a n-type semiconductor but an ionic conductor. Therefore, the ultra-fine LSGM powder prepared using this improved citric acid method had the characteristic property of a solid oxide electrolyte and can be used for the fabrication of a ultra-thin LSGM membrane supported on a porous electrode substrate.

CONCLUSIONS

By the improved citric acid method, i.e., EDTA-citric acid combined complex method, ultra-fine LSGM powder can be easily prepared. In this method, EDTA is added to the mixed solution of the metal nitrates as a complexant and citric acid as aid complexing and gelatification agent. $\text{NH}_4\text{NO}_3$ is added as a foam-forming agent. The addition of $\text{NH}_4\text{NO}_3$ has a strong effect on the crystallization initial temperature and the granular distribution of the electrolyte powder. Adding $\text{NH}_4\text{NO}_3$ into the mixed solution can further decrease the synthesizing temperature of LSGM and the average particle sizes of the resultant products. By adopting this improved synthesis technique, the synthesizing temperature of LSGM can be decreased from 1500°C to 1120°C and ultra-fine LSGM powder can also be obtained. The LSGM ultra-fine powder has an acceptable electrical conductivity and a high ionic transference number, making it fit for the fabrication of a dense LSGM ultra-thin membrane on an electrode substrate.

ACKNOWLEDGEMENT

This work has been supported by New Energy and Industrial Technology Development Organization (NEDO) of Japan and National Science Foundation (NSF) of China.
REFERENCES

(1) N. Q. Minh, *J. Am. Ceram. Soc.* 76, 563 (1993)
(2) Y. Jiang, W. Li, S. Wang, *Progresses in Chemistry* (Chinese), 9, 387 (1997)
(3) S. C. Singhal, in *Solid Oxide Fuel Cells VI*, S. C. Singhal, M. Dokiya, Editors, PV 99-19, p. 39, The Electrochemical Society Proceeding Series, Pennington, NJ (1999)
(4) A. Casanova, *Journal of Power Sources*, 71, 65 (1998)
(5) K. Choy, W. Bai, S. Charojrochkul, B. C. H. Steele, *Journal of Power Sources*, 71, 361 (1998)
(6) J. P. P. Huijsmans, F. F van Berkel, G. M. Christie, *Journal of Power Sources*, 71, 107 (1998)
(7) T. Ishihara, H. Matsuda, and Y. Takita, *J. Am. Chem. Soc.*, 116, 3801, (1994)
(8) P. Huang and A. Petric, *J. Electrochem. Soc.*, 143, 1644 (1996)
(9) J. W. Stevenson, T. R. Amstrong, D. E. McCready, L. R. Pederson and W. J. Weber, *J. Electrochem. Soc.*, 144, 3613 (1997)
(10) K. Tabata and M. Misono, *Catalysis Today*, 8, 249 (1990)
(11) W. Luan, L. Gao and J. Guo, *J. Advanced Materials*, 31, 3 (1999)
(12) T. Zhang, F. Peng and C. Tang, *J. Inorganic Materials* (Chinese), 11, 435 (1996)
(13) L. V. Solov’va, I. A. Bashmakov, V. P. Novikovetc and F. N. Kaputskii, *Inorganic Materials*, 31, 1416 (1995)

Fig. 1 Preparation Procedure of LSGM powder by Improved Citric Acid Method

364 Electrochemical Society Proceedings Volume 2001-16
Fig. 2, Thermogravimetric and Differential Thermal Analysis of LSGM precursor obtained by improved citric acid synthesis technique

Fig. 3, Infrared Spectroscopy of LSGM samples which were treated at various temperatures for 180 min

Fig. 4, XRD patterns of the resultant products derived by sintering the LSGM precursor at various temperatures for 180 min, which was prepared by improved citric acid method
Fig. 5, Thermal Grametry and Differential Thermal Analysis of LSGM precursor obtained by mixing La$_2$O$_3$, SrCO$_3$, Ga$_2$O$_3$ and MgO

![Thermal Grametry and Differential Thermal Analysis](image)

Fig. 6, XRD patterns of the resultant products derived by sintering the LSGM precursor at various temperatures for 180 min, which was prepared by mixing La$_2$O$_3$, SrCO$_3$, Ga$_2$O$_3$ and MgO

![XRD patterns](image)

Fig. 7, Thermal Grametry and Differential Thermal Analysis of LSGM precursor obtained by improved citric acid synthesis technique with addition of NH$_4$NO$_3$

![Thermal Grametry and Differential Thermal Analysis](image)
Fig. 8, TEM pictures of LSGM powders obtained by sintering the precursor for 180 min at 1200°C and 1300°C respectively. This precursor was prepared by improved citric acid method with addition of NH₄NO₃.

Fig. 9, Temperature dependence of the electrical conductivity (in Air) of LSGM prepared by improved citric acid method with addition of NH₄NO₃.

Fig. 10, Oxygen partial pressure dependence of the electrical conductivity (at 800°C) of LSGM prepared by improved citric acid method with addition of NH₄NO₃.