CHARACTERIZATION OF ANODE SUBSTRATES
AND SUPPORTED ELECTROLYTE THIN FILMS FOR
INTERMEDIATE TEMPERATURE SOLID OXIDE FUEL CELLS

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ABSTRACT
The relationship between microstructure, electrical conductivities of
La$_{0.5}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_{3-d}$ (LSGM) + NiO anode substrates and their
compositions has been studied. Anode substrate with 60% NiO content
had a preferable microstructure. Electrical conductivity of a reduced
substrate with a low NiO content increased rapidly with a. c. impedance
measuring time and changed from electronic to ionic in conductivity
character. For the reduced substrates with a high NiO content, electrical
conductivity increased slowly with measuring time and showed metallic
conducting behavior from the beginning. A dense LSGM film with a
thickness of 20-50 µm was successfully prepared on this substrate using a
costly effective wet chemical-physics method. On the surfaces of LSGM
thin films fabricated by non-restraint sintering method, large flat grains
were formed and cracks appeared along the grain boundaries after reduced
in H$_2$. Just small grains contacting with each other tightly could be
observed on the surfaces of LSGM thin films fabricated by iso-static
pressure sintering method, and no cracks appeared along the grain
boundaries after reduction in H$_2$. To avoid reaction between LSGM in the
films and the NiO in the substrates, a Ce$_{0.8}$Sm$_{0.2}$O$_{3-d}$ interlayer with a
thickness of 2-5 µm was successfully fabricated, forming a sandwich
structure.

INTRODUCTION
There are two commonly adopted routes to lower SOFC operating temperature. One
way is fabricating dense YSZ thin films supported on anode or cathode substrates to
decrease internal resistance loss. Another way is using alternative oxides as electrolytes
instead of YSZ. The oxide-ion conductivity of these new electrolytes at or below 800°C
should be comparable with that of YSZ at 1000°C (1).
Great progresses have been made in the investigation of intermediate temperature solid
oxide fuel cells with supported YSZ thin films (2,3,4). Plasma spray, chemical vapor
deposition (CVD), electrochemical vapor deposition (EVD) are usually used methods for
the preparation of YSZ thin films. However, it is not only expensive but also difficult to
fabricate large area electrolyte thin films with these techniques. Successful fabrications
of dense YSZ films using wet processes have been reported by some SOFC investigation groups (5,6,7).

On R&D of new solid oxide electrolytes, $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_3$ with perovskite structure, which was firstly synthesized by Tatsumi Ishihara et. al. in 1994, attracts more and more attentions these years (8). It is a promising material for intermediate temperature solid oxide fuel cells due to its high ionic conductivity and high ionic transference number. However, with the operating temperature decreased further, the resistance drop of the internal electrolyte turns to be main limitation to the output power density. If supported LSGM thin films is successfully made on porous electrode substrates, operating temperatures of SOFC can be decreased to 500-600°C, which will facilitate SOFC to compete automobile, military submarine and other mobile power source markets.

In this investigation, $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ (LSGM) was synthesized with traditional solid-state reaction route and characterized by XRD and a. c. impedance spectroscopy techniques. A dense LSGM film was successfully prepared on an LSGM + NiO substrate with a wet chemical-physics method. Shrinkages of substrates with different NiO contents were investigated. Effect of NiO content on the porosity, pore radius distribution in the substrate and its electrical conductivity was examined in details. The relationship of electrolyte film quality, surface morphology and the content of NiO in the substrates were also investigated.

**EXPERIMENTAL**

**Synthesis and Characterization of Electrolyte LSGM**

LSGM was prepared by traditional solid-state reaction route. $\text{La}_2\text{O}_3$ (purity 99.99%, Shanghai Yuelong Non-ferrous Metal Corporation), $\text{SrCO}_3$ (purity 99.99%, Shanghai No. 1 Chemical Plant), $\text{Ga}_2\text{O}_3$ (purity 99.99%, Shanghai Chemical Packing Corporation), $\text{MgO}$ (purity 99.9-100.0%, Shanghai Tongji Institute of Trace Elements) were used as the starting materials. The mixture was thoroughly pulverized and then sintered at 1000°C for 2 h to get a precursor powder. Part of the precursor was pressed into disks under an axial pressure of 17.76 MPa. These disks were calcined at 1500°C for 15 h and then cut into long bars for the measurement of the electrical conductivities. A.c. impedance technique was used to measure the electrical conductivities of LSGM under different temperatures (from 400°C to 900°C) and different oxygen partial pressures (from $3.0 \times 10^{-23}$ MPa to $9.9 \times 10^{-2}$ MPa). 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 includes a Potentiostat/Galvanostat (EG&G Model 173 with Current Converter Model 376), a Lock-in Amplifier (EG&G Model 5204), a Function Generator (Good Will Instrument Corporation Limited, Model GFG-8109G). Some LSGM disks were ground into fine powder for the XRD determination of their crystal structure. A powder XRD pattern was collected on a model D-MAX-RB Powder X-ray Diffractometer using Cu Kα radiation.

**Preparation and Characterization of LSGM + NiO Anode Substrates**

LSGM and commercial NiO (Reagent for electric ceramic, J. T. Baker, USA) were thoroughly mixed in different ratios. Proper amount of organic additives were added
into a sample and then ground until a dry powder was obtained. The mixing powder was pressed into disks under an axial pressure of 17.76 MPa. The green disks were sintered at 1500°C for 15 h and then reduced in dilute H₂ (20% H₂, 80% Ar) at 900°C for 400 min. The reduced samples were used to investigate the relationship between porosity, pore radius distribution, specific pore surface-area and the NiO content in a substrate under operating conditions of SOFC. Porosity and pore specific volume etc. of a reduced LSGM + NiO substrate was measured by mercury method. Some substrates were cut into long bars and Pt electrodes were made on two ends of the bars. These samples were used for the characterization of the electrical conductivity using a c. impedance technique mentioned above after being reduced in diluted H₂ at 900°C for 8 h.

**Fabrication and Morphological Investigation of Dense LSGM Films Supported on Porous LSGM + NiO Substrates**

Organic dispersants and ethanol were added into LSGM precursor to form a uniform and viscous dispersion. This dispersion was dipped on one side of a substrate and a supported green membrane was formed after those solvents in the film evaporated. The samples were sintered at 1500°C for 15 h to form a dense LSGM film with a thickness of 30-50μm. The substrate disks with LSGM films were reduced in dilute H₂ at 900°C for 400 min. Scanning electron microscope (SEM) was used to observe the surface morphologies and cross sections of the reduced samples. An interlayer of Ce₀.₈Sm₀.₂O₁.₈ (SDC) was also prepared between a substrate and a LSGM film, forming a sandwich structure, in order to prevent the reactions between LSGM in the films and NiO in the substrates.

**RESULTS AND DISCUSSION**

**Properties of Electrolyte LSGM**

XRD analysis result shows that the LSGM synthesized by solid-state reaction had a pure perovskite structure. From a c. impedance spectroscopy, electrical conductivity of LSGM could be derived. The electrical conductivity of LSGM was 0.0863 S-cm⁻¹ at 800°C, which was comparable with that of YSZ at 1000°C.

From the electrical conductivity of LSGM in air at different temperatures, we could get the activation energies (Ea) of LSGM electrical conductivity. It was 0.67 eV above 750°C, 0.86 eV in the range from 525°C to 750°C and 1.08 eV below 525°C. The increase of Ea with the decrease of temperature could be related to the association of oxygen vacancies and dopant cations in the electrolyte. Table 1 shows the oxygen partial pressure dependence of electrical conductivity of LSGM. It should be noted that the last two conductivity data were measured in CO and H₂ respectively and the oxygen partial pressures were derived from Nernst equation. Except in H₂, electrical conductivity of LSGM kept almost constant in a wide range of oxygen partial pressures.

**Effect of NiO content on the sintering shrinkage, porosity and microstructure of a LSGM + NiO anode substrate**

Table 2 shows the disk shrinkage rates of the LSGM + NiO substrates with different proportion of NiO after being sintered at 1500°C for 15 h. It could be observed that with
the increase of the proportion of NiO, the sintering shrinkage decreased. From the viewpoint of shrinkage compatibility, the decrease of NiO in a substrate was preferable to the formation of a supported electrolyte film. However, electrode activity and electrode microstructure are two other important aspects to be considered when we design a new electrode for a SOFC.

Table 3 shows the relationship between porosity, average pore radius, pore radius distribution, specific pore volume and specific surface-area of a reduced NiO+LSGM substrate with the NiO ratio before reduction. For the substrate with 20% NiO, porosity, etc. were all zero. This indicated that sample 1 could not meet the basic requirements for the SOFC electrodes. For sample 4 with 80% NiO, although the porosity and average radius of pores reached to 32.8% and 119.22 nm respectively, its specific volume of pores was lower than that of sample 3 and 4. Compared with substrate 2, pore radius distribution in substrate 3 was more preferable. There were 70.22% middle pores with radius between 32.25 and 110.82 nm and 29.78% large pores with radius larger than 110.82 nm, which would facilitate gas diffusion in the anode substrate. Because of its large specific volume and specific area of pores, the TPB where electrode reactions took place was increased in substrate 3. Therefore, the optimal NiO content in NiO+LSGM substrate was 60% in regard to its microstructure.

**Relationships of the Electrical Conductivities of the Reduced LSGM + NiO anode substrates and their NiO contents at various temperatures**

The electrical conductivities of sample 1 and 2 were very unstable. At the beginning of the measurement, they were very low and comparable with that of electrolyte LSGM. The electrical conductivity increased with the measuring time and reached a stable value in about 14-15 h. At this time, the electrical conductivities of these samples were hundreds times of those of the fresh samples. After treated in H2 without out signals applied for the same period, we measured the conductivities of sample 1 and 2 and found that they changed very small with time. This indicated that the increase of the electrical conductivities was associated with the alternative signals added to the samples during the a.c. impedance measurements. LSGM grains contacted to form a continuous framework and NiO dispersed in pores apart from each other in a sintered sample with a low NiO content. After reduced in H2, the reduction product Ni particles did not contact with each other and the most important contribution to the electrical conductivity came from the electrolyte. On the inducement of an alternative signal, Ni particles redistributed in the LSGM framework at high temperatures and contributed to the total conductivity more and more with the measuring time. Finally the reduced substrates with low NiO content exhibited metallic electrical conductive characters. This process not only increased the electrical conductivity but also increased the TPB in the electrodes. For substrate 3 and 4 with high NiO content, their electrical conductivities were high from the very beginning and changed very small with the measuring time. Ni particles in a reduced NiO+LSGM substrate with high proportion of NiO contacted with each other, forming an electron-transferring path, which led to a high electrical conductivity.

Fig. 1 shows the temperature dependence of the electrical conductivities of the NiO+LSGM substrates with different proportion of NiO. It should be noted that the electrical conductivities of substrate 1 and 2 in this figure were the stable data measured after the relaxation of the samples was completed in about 15 h. At a given temperature, the electrical conductivities of the anode substrates increased with the proportion of NiO. The absolute electrical conductivities of these substrates in H2 were high enough to be
used as SOFC anodes. Electrical conductivities of anode substrates with different proportion of NiO decreased with the increase of temperatures and exhibited metallic conductive behavior. The electrical conductivity of substrate 1 and 2 with low NiO content decreased slowly with the increase of temperature. Electrical conductivity of substrate 3 was nearly the same as that of substrate 4 at 400°C and decreased rapidly when temperature increased at low temperature. However it changed very small when temperature increased from 700°C to 800°C. No relaxation effect of electrical conductivity was observed for substrate 3.

**Fabrication and Structural Characterization of LSGM Thin Films Supported on Porous LSGM + NiO substrates**

To further investigate the compatibility between electrolyte films and anode substrates, films of LSGM precursor supported on NiO+LSGM substrates with different proportion of NiO were fabricated and then sintered at 1500°C for 15 h for the examination of their deformation and quality. It could be observed that the less the proportion of NiO in the substrates, the better the shrinkage compatibility between LSGM films and the substrates. Substrates with low percentage of NiO kept flat and LSGM films with large flat grains on their surfaces were formed after being sintered. The LSGM film surfaces were smooth and the grain boundaries were clear. On the substrates with high percentage of NiO, the shrinkage of the LSGM films was quite different with that of the substrates, which led to a serious deformation of the samples. These disks curved up to the sides of the electrolyte films due to higher sintering shrinkage of LSGM. The deformation of substrate 4 with 80% NiO was the most serious one among these four samples we investigated.

To fabricate dense LSGM films on NiO + LSGM substrates, a contrast experiment with iso-static sintering technique was carried out. During the iso-static sintering process, a 0.2 MPa axial pressure was applied on a sample, which could effectively prevent the deformation of the substrates during sintering process and affected the surface morphology of LSGM film supported on the substrate. Scanning Electron Microscope (SEM) was used for the observation of the surfaces and cross sections of supported LSGM films after being reduced in dilute H2 at 900°C for 400 min.

Fig 2 shows the SEM photographs of the surface morphologies of LSGM films on various substrates prepared using non-restraint sintering processes. On the surfaces of these electrolyte films, an inter-grain product was formed between large flat grains with regular shapes. However, no LSGM films with a clear surface structure could be observed on substrate 4 with 80% NiO because of significant shrinkage difference between the substrate and the electrolyte film. There appeared some white spots on the surface of the LSGM film supported on substrate 1. Their compositions were not clear yet.

Fig. 3 shows the surface morphologies of LSGM films supported on various substrates that were fabricated with an iso-static sintering process. There were only relatively small grains with clear grain boundaries on the surfaces of LSGM films and no inter-grain phases formed between these grains. The morphology of the film surface on substrate 4 was the worst one among these four samples but was much better than that prepared with non-restraint sintering process on the same kind of substrate. The obvious difference of the surface morphologies of LSGM films prepared with two different sintering processes was related to the sintering resistance and sintering force during the sintering process, which included two processes, phase formation and film formation. The phase formation process of LSGM was a typical solid-state reaction. At high temperatures, oxide particles
reacted at their interfaces to form a new phase. With the reaction proceeded, the reaction resistance increased. To make those oxides reacted with each other thoroughly, quite a long reaction time was needed. So we sintered samples at 1500°C for 15 h to acquire pure phase LSGM films in our investigations.

From cross view SEM of LSGM films supported on the anode substrates prepared by the iso-static sintering process, we could learn that the thickness of the LSGM films was about 50 μm.

Fig. 4 shows the difference of the surface morphologies of supported LSGM films prepared by two different sintering processes, which had been reduced in H2. From the SEM photographs we can see that there appeared cracks along grain boundaries on the surfaces of LSGM films fabricated on substrate 2 and 3 with non-restraint sintering process. The volume changes associated with the reduction of NiO in the substrates led to this phenomenon. With the increase of NiO proportion in the substrates, the cracking was getting more and more serious. For the supported LSGM films prepared by iso-static pressure sintering process, there were no cracks along the grain boundaries after NiO in the substrates was reduced to Ni in dilute H2. The stress that came from the reduction of NiO in a substrate was dispersed by the grain boundaries along those fine LSGM grains, which would decrease the stress on a single grain boundary.

Although a dense LSGM film could be fabricated on a NiO + LSGM substrate, the open circuit voltage was still low. XRD analysis showed that NiO reacted with LSGM to form a new phase above 1200°C. This new phase was an electronic-ionic mixing conductor which would form an internal short-circuit in a SOFC single cell. To avoid direct contact between NiO in the substrate and LSGM in the film, a SDC interlayer was fabricated to form a sandwich structure. The thickness of this interlayer was about 2-5 μm. With this interlayer, the open circuit voltage could be raised to about 1 V at 800°C when using H2 as fuel and O2 as oxidant. Another function of this interlayer was to decrease the anode overpotential, leading to a higher power output performance.

CONCLUSIONS

High strength anode substrates can be fabricated from the mixtures of LSGM precursor and NiO by a high temperature sintering process. After NiO in the substrate is reduced to Ni in reducing atmosphere, a porous anode cermet is formed. The addition of LSGM into NiO can adjust the sintering shrinkage of a NiO + LSGM substrate to make it compatible with that of the electrolyte film supported on it and expand the TPB from the interface between the substrate and the electrolyte film to entire anode substrate. The proportions of LSGM and NiO have a dramatic effect on the sintering shrinkage and microstructure of the substrate, including porosity, pore radius distribution, average pore radius, pore specific area and pore specific value, etc. Anode substrate with 60% NiO is preferable for SOFC anode when considering its microstructure.

Electrical conductivity of a reduced anode substrate increases with the NiO proportion. Electrical conductivity of a fresh substrate after reduction in H2 is very low and exhibits ionic conductive character. However under the induction of an alternative signal, the electrical conductivity increases to a very high value after 14-15 h and then showing metallic conductive behavior. But for a reduced substrate with high NiO content, its high electrical conductivity changes very small with the measuring time and shows ionic conductive character from the beginning.

The quality of LSGM films supported on the anode substrates is affected by the
microstructure of the substrates. Except on the substrate with 80% NiO, grains on the surfaces of LSGM films prepared by non-restraint sintering process are larger than that by iso-static sintering process. When NiO in the substrates is reduced to Ni by H₂, there appear clear cracks along the grain boundaries on the surfaces of LSGM films fabricated by non-restraint sintering process and for the LSGM films fabricated by iso-static sintering process, those grains on their surfaces keep contacting tightly after being reduced. An interlayer of SDC can not only avoid the reaction of NiO in the substrates and the LSGM in the electrolyte films but also decrease the anode overpotential, which in turn improve the output performance of a SOFC single cell.

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Table 1 Electrical conductivity of LSGM at 1073K as a function of oxygen partial pressure

| $P_{O_2}$/MPa | $\log\sigma$/S·cm$^{-1}$ | $P_{O_2}$/MPa | $\log\sigma$/S·cm$^{-1}$ |
|--------------|----------------|--------------|----------------|
| 9.9x10$^{-2}$ | -1.40          | 4.1x10$^{-3}$ | -1.56          |
| 5.1x10$^{-2}$ | -1.41          | 5.1x10$^{-22}$ | -1.57          |
| 1.3x10$^{-2}$ | -1.47          | 3.0x10$^{-23}$ | -1.37          |

Table 2 Relationship between radial shrinkage rates of sintered anode substrates and their NiO contents

| Sample number | NiO content/% | Radial shrinkage rate/% |
|---------------|---------------|-------------------------|
| 0             | 0             | 29.32                   |
| 1             | 20            | 28.18                   |
| 2             | 40            | 26.82                   |
| 3             | 60            | 25.45                   |
| 4             | 80            | 24.18                   |

Table 3 Relationship between porosity, mean pore radius, pore radius distribution, specific pore volume, specific surface-area of reduced LSGM+NiO substrates and NiO content in the substrates before reduction

| Sample number | 1 | 2 | 3 | 4 |
|---------------|---|---|---|---|
| NiO content/% | 20| 40| 60| 80|
| Porosity/%    | 0 | 19.8| 26.7| 32.8|
| Mean pore radius/nm | 0 | 35.44| 71.49| 119.22|
| $>110.82$ nm  | 0 | 0 | 29.78| 81.16|
| Pore radius distribution/% | 32.25-110.82 nm | 0 | 95.45 | 70.22 | 17.40 |
| 10.05-31.25 nm | 0 | 4.55 | 0 | 1.44 |
| Specific pore volume/ml·g$^{-1}$ | 0 | 0.024 | 0.047 | 0.063 |
| Specific surface-area/m$^2$·g$^{-1}$ | 0 | 1.34 | 1.32 | 1.05 |

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Fig. 1 Relationship between conductivities of reduced NiO + LSGM substrates (S·cm⁻¹) and temperatures
(a) Substrate 1 with 20% NiO  (b) Substrate 2 with 40% NiO
(c) Substrate 3 with 60% NiO  (d) Substrate 4 with 80% NiO

Fig. 2 SEM photographs for surfaces of supported LSGM thin films fabricated by non-restraint sintering method
(a) Film on substrate 1 with 20% NiO  (b) Film on substrate 2 with 40% NiO
(c) Film on substrate 3 with 60% NiO  (d) Film on substrate 4 with 80% NiO
Fig. 3 SEM photographs for surfaces of supported LSGM thin films fabricated by isostatic-pressure sintering method
(a) Film on substrate 1 with 20% NiO
(b) Film on substrate 2 with 40% NiO
(c) Film on substrate 3 with 60% NiO
(d) Film on substrate 4 with 80% NiO

Fig. 4 SEM photographs for surfaces of supported LSGM thin films fabricated by different sintering methods after reduction in diluted H₂
(a) Film fabricated by non-restraint sintering method on substrate 2 with 40% NiO
(b) Film fabricated by non-restraint sintering method on substrate 3 with 60% NiO
(c) Film fabricated by iso-static pressure sintering method on substrate 2 with 40% NiO
(d) Film fabricated by iso-static pressure sintering method on substrate 3 with 60% NiO