



Fabrication of apatite-type lanthanum silicate films and anode supported solid oxide fuel cells using nano-sized printable paste

Hideki Yoshioka^{a,*}, Hiroyuki Mieda^b, Takahiro Funahashi^b, Atsushi Mineshige^b, Tetsuo Yazawa^b, Ryohei Mori^c

^a Hyogo Prefectural Institute of Technology, Suma-ku, Kobe, Hyogo 654-0037, Japan

^b Department of Materials Science and Chemistry, Graduate School of Engineering, University of Hyogo, Himeji, Hyogo 671-2201, Japan

^c Fuji-Pigment Co. Ltd., Kawanishi, Hyogo 666-0015, Japan

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Abstract

Apatite-type lanthanum silicate based films have attracted significant interests to use as an electrolyte of solid oxide fuel cells (SOFCs) working at intermediate temperature. We have prepared Mg doped lanthanum silicate (MDLS) films on NiO–MDLS cermet substrates by spin coating and sintering of nano-sized printable paste made by beads milling. Changes in crystal structure and microstructure of the paste films with the sintering temperature have been investigated to show that porous network structure with a grain growth evolves up to 1300 °C, whereas densification occurred above 1400 °C. Anode supported SOFCs using the pasted MDLS films were successfully fabricated: an open circuit voltage of 0.91 V and a maximum power density of 150 mW cm⁻² measured at 800 °C were obtained with the electrolyte film sintered at 1500 °C.

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1. Introduction

Solid oxide fuel cells (SOFCs) have attracted great interest as clean and high efficient electrical power sources. Reduction of operating temperature of SOFCs down to intermediate temperature (500–700 °C) gives significant advantages such as wider ranges of material selection, longer life and lower manufacturing costs.^{1,2} Development of solid electrolytes which exhibit high ionic conductivity at reduced temperature is one of the key issues for the commercialization of intermediate temperature solid oxide fuel cells (IT-SOFCs). However, ionic conductivity of a common SOFC solid electrolyte, yttria stabilized zirconia (YSZ) rapidly reduces as temperature decreases. Numbers of research have been done searching for solid electrolyte materials which exhibit high ionic conductivity even at intermediate temperature range such as doped ceria³ and doped lanthanum gallate⁴ type solid electrolyte materials.

Nakayama et al. have first demonstrated that apatite-type lanthanum silicate exhibits high ionic conductivity and high oxide-ion transport number even at intermediate temperature range.⁵ Ionic conductivity of the lanthanum silicate was found to be enhanced by introduction of excess oxide ions⁶ and cation doping into La or Si sites.^{7,8} Among them, Al doping into the Si site of oxide-ion excess lanthanum silicate gives an marked increase: these apatites showed ionic conductivity of 17–30 mS cm⁻¹ at 700 °C^{9–11} which were higher than YSZ. We have reported that ionic conductivity of lanthanum silicate can be also enhanced by doping Mg into the Si site¹² and has been attempted to be utilized for a solid electrolyte of IT-SOFCs.¹³ Mg doped lanthanum silicate (MDLS) exhibits high ionic conductivity comparable to Sr and Mg doped lanthanum gallate at temperatures less than 550 °C.¹⁴ SOFCs using doped lanthanum silicate ceramic electrolytes have shown moderate power densities of 125–250 mW cm⁻¹ at 800 °C.^{14–16} However, fabrication of lanthanum silicate ceramics based SOFC for practical use is still difficult because of the high sintering temperature of lanthanum silicate ceramics (>1600 °C), which prevent us from preparing dense electrolyte films with low manufacturing costs. To overcome this obstacle,

* Corresponding author at: 3-1-12, Yukihiro-cho, Suma-ku, Kobe, Hyogo 654-0037, Japan. Tel.: +81 78 731 4302; fax: +81 78 735 7845.

E-mail address: hide@hyogo-kj.jp (H. Yoshioka).

we have started the research to prepare thin films of lanthanum silicates directly on the electrode substrates as electrode supported-type SOFCs. There are some previous researches to make lanthanum silicate films by sol–gel method,¹⁷ thermal spraying,^{18–20} sputtering^{21,22} and tape casting.²³ To the best of our knowledge, none of these researches, however, have succeeded in making highly conductive lanthanum silicate films and in preparing electrode supported SOFCs. There is only one paper published by our group reporting the fabrication of anode supported SOFCs using thermal sprayed MDLS films on NiO–MDLS cermet anodes.²⁴ We have shown in this paper that the thermal sprayed MDLS films could be crystallized above 800 °C to be an oxide-ion conductor. The SOFC thus obtained showed a maximum power density of 80 mW cm⁻² at 800 °C with a common (La_{0.6}Sr_{0.4})(Co_{0.8}Fe_{0.2})O_{3-δ} (LSCF) cathode material.

The purpose of this study is to develop a more versatile and cost-effective procedure to make SOFCs having high power densities at intermediate temperature by using highly conductive MDLS electrolyte films. We have successfully fabricated dense electrolyte films from printable paste consisting of nano-sized MDLS particles made by bead milling technique. This paper reports fabrication of dense MDLS electrolyte films by spin coating of the paste and application to anode supported SOFCs. Optimization of the cell structure and the fabrication procedure including electrode microstructure control to increase power density is under investigation and the results will be published elsewhere.

2. Experimental

2.1. Preparation of nano-sized MDLS paste

MDLS powder with a composition of La_{0.8}Si_{5.7}Mg_{0.3}O_{26.4} was prepared by a conventional solid state reaction of La₂O₃, SiO₂ and MgO powders at 1600 °C, followed by grinding and sieving according to the particle sizes. Powders with particle sizes less than 10 μm are used for fabrication of both MDLS paste and anode substrates.

MDLS printable paste for spin coating was prepared by mixing the powder and polyoxyethylene sorbitan tristearate as a dispersant (Kao Corporation, Japan) in terpineol (Arakawa Chemical Industries Co. Ltd., Japan) with zircon beads using a stirring machine rotating for 30 min at 3500 rpm. The viscous paste was made by combining 21 g of MDLS powder with 2 g of dispersant and 47 g of terpineol. Then 3 g of ethyl cellulose (Nisshin Kasei Co. Ltd., Japan, *M*_w 20,000) was added to 45 g of sol slurry as a binder to increase viscosity and stirred for an additional 30 min at 2000 rpm to completely dissolve ethyl cellulose.

Thermogravimetry (TG) and differential thermal analysis (DTA) were performed using a TG-DTA system (Thermoplus EVO TG-8120, RIGAKU Corp., Japan) to evaluate the thermal properties of the MDLS paste. Air flow rate and temperature scanning rate were set to 300 ml min⁻¹ and 20 °C min⁻¹, respectively.

2.2. Preparation and characterization of MDLS paste films

NiO and MDLS powders were mixed in 6:4 in weight ratio and pressed into disks of 13 mm in diameter and 1.5 mm in thickness. They were sintered at 1400 °C for 4 h to obtain cermet anode substrates. MDLS pastes were spin-coated on the cermet anode substrates with a spinning rate of 5000 rpm for 30 s. They were dried at 180 °C for 10 min and then heated at 500 °C for 10 min to burn out organic component. After repeating this procedure for 4 times, the MDLS films on the anode substrates were finally sintered for 4 h at various temperatures between 1000 and 1500 °C.

Phases in the films were investigated by X-ray diffraction (XRD) method using a powder diffractometer (RAD-RU, Rigaku Corp.) with Cu Kα radiation of 40 kV–200 mA. Film structures were examined by a field-emission type scanning electron microscope (SEM) (Sirion, FEI company) with an acceleration voltage of 5 or 10 kV.

2.3. Fabrication and evaluation of anode supported SOFCs

Anode supported single cells were obtained by screen-printing La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃ (LSCF) cathode paste to the electrolyte film surfaces and heated at 1000 °C. The cathode paste was prepared by mixing LSCF powder in terpineol solvent. Then, Pt paste electrodes of 8 mm in diameter were painted on both LSCF and anode substrate faces and fired again at 1000 °C to ensure the electrical contact. This single cell was applied to SOFC evaluation equipment and heated to 1000 °C to complete glass ceiling and set down to 800 °C. Thus, oxygen was supplied to cathode side and H₂–Ar gas was supplied to anode side to reduce NiO in the anode substrates. After open circuit voltages (OCV) became stable, current–voltage (*I*–*V*) characteristic curves were measured using a galvanostat and an electrometer, which then gave current–power densities (*I*–*P*) characteristic curves. AC impedances at an open circuit state were measured by a BAS ALS-760C impedance analyzer with frequencies ranging from 100 kHz to 10 mHz. *I*–*V* characteristic curves and AC impedance measurements were performed at 800, 700 and then 600 °C.

3. Results and discussion

3.1. Preparation of MDLS paste films

Fig. 1 shows TG–DTA curves of the MDLS paste. The TG curve revealed that approximately a half of organic solvent, terpineol, was evaporated until 250 °C followed by a gradual decomposition of dispersing chemical and resin observed up to 450 °C. Exothermic DTA peaks of 401 °C and 422 °C are ascribed to decompositions of ethyl cellulose and dispersing chemical, respectively. Thus, complete decomposition of dispersing chemical and resin would be expected when 500 °C was applied after spin coating.

Fig. 2 shows pictures of (a) an anode substrate and (b) a film surface after spin coating and heating at 500 °C for 4 times. Fig. 2(c)–(h) are film surfaces after heated at 1000–1500 °C.

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