Intermediate-temperature operation of solid oxide fuel cells (IT-SOFCs) with thin film proton conductive electrolyte

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Abstract. A novel solid oxide fuel cell (SOFC) structure, which is fabricated on a Pd-plated porous stainless steel substrate, was proposed for low-temperature SOFC operation. The surface of the substrate was covered with Pd layer without any pores, which reduces the difficulty of depositing thin film electrolyte on the porous substrate. A 1.2-μm thick proton conductive Sr(Zr0.8Y0.2)O3−δ (SZYO) layer and the cathode of a 100-nm thick (La0.6Sr0.4)(Co0.2Fe0.8)O3−δ (LSCF) layer were deposited on the Pd-plated substrates by the pulsed laser deposition (PLD) method. The low temperature operations at 400 and 450 °C were demonstrated with proposed SOFC cells.

1. Introduction

Solid oxide fuel cells (SOFCs) are considered to be one of the candidates for future energy sources because of its high electricity generating efficiency. However, its high operating temperatures of 800-1000 °C brings higher apparatus cost and difficulty in its quick start-up, which prevents enlarging its applications, especially for the home uses. Thus, achieving operating temperatures below 600 °C is considered to be a key for solving these issues.

To achieve the lower operating temperatures, the reduction of the electrolyte thickness is quite effective. However, thinning the electrolyte requires a substrate that must possess fuel gas permeability. Thus, porous substrates are usually used, which makes depositing thin films electrolyte quite difficult.

In 2005, Ito et al. reported good SOFC operations below 600 °C with using a thin electrolyte less than 1 μm in thickness [1]. They used palladium (Pd) foils as a substrate to avoid the difficulty of the
deposition. However, the cost of the substrate is expensive and it is not realistic for the commercially available SOFCs.

In order to resolve this issue, we have proposed to use a Pd plated porous stainless-steel instead of using solid Pd as a substrate [2,3]. Figure 1 shows a schematic of our proposed SOFC cell structure. As the top surface of the substrate is fully covered with the planer Pd, we can use a variety of deposition techniques of oxide thin films, such as pulsed laser depositions (PLD) method, Sputtering method, and Sol-gel method, etc with a lower substrate cost than that of Ito et al.’s. We adopted PLD method for fabricating proton conductive electrolyte of Sr(Zr0.8Y0.2)O3-δ (SZYO) and cathode layer of (La0.6Sr0.4)(Co0.2Fe0.8)O3-δ (LSCF) on the Pd-plated substrate.

In this study we describe the fabrication procedure of our novel SOFCs and its low temperature operations at 400 and 450 °C.

2. Experimental procedure

2.1 Fabrication of SOFC cells

A fabrication condition of Pd plated porous stainless substrates is described elsewhere [3]. A pressurized hydrogen (H2) gas was used to measure H2 permeability.

SZYO and LSCF layers were deposited by PLD method, using an excimer laser with a wavelength of 248 nm. Target materials of SZYO and LSCF used in this study were prepared by spark plasma sintering. The SZYO and LSCF films were deposited on Pt/SiO2/Si substrate (abridged as Pt/Si sub. in this paper) for evaluating crystallinity and conductivity and Pd-plated stainless steel substrate to fabricate the SOFC structure.

2.2. Characterization

Crystallinity of the deposited films was evaluated by X-ray diffractions (XRD) with 0-2θ scans. Deposition conditions of PLD method were optimized by the XRD to obtain single phase of SZYO and LSCF with high crystallinity.

Arrhenius plots for proton conductivity of the cell were obtained from measuring alternating-current impedance in dry and wet Ar atmospheres by 4194A (Agilent Technologies) impedance analyser. Conditions of alternating-current impedance measurement were as follows: measurement frequency of 100 to 400 MHz, constant current of 20 mA, humidification temperature of 40 °C for wet Ar.

The single-cell performances, current density - cell voltage and current density - power density curves, were measured by an evaluation system, TOYO-Auto PEM (TOYO Corporation) installed by TOYO TFT integrated software. Both sides of the sample cell were connected to TOYO-Auto PEM system by Pt paste and Pt wire. The power generation properties were evaluated under the following test conditions: cell temperature at 400 °C and 450 °C, cathode humidification temperature of 25 °C, anode humidification temperature of 25 °C, hydrogen feed rate of 0.15 L/min, and air feed rate of 0.10 L/min.

3. Results and discussion

3.1 H2 permeability

Figure 2 shows the H2 permeability of the Pd-plated substrate in comparison with a 200 μm-thick Pd sheet. A larger permeability of the substrate than that of Pd sheet was observed at 300 and 400 °C. This was brought from the thinner Pd layer of 5-15 μm in the substrate. On the contrary, a lower permeability of the substrate at higher temperatures of 500 and 600 °C was observed. This might come
from the degradation of the Pd layer because of diffusion of alloy elements from the stainless steel. We need more improvement of the substrates to suppress Pd layer degradation at higher temperatures.

3.2 Optimization of PLD conditions
As for the PLD deposition, we examined oxygen (O₂) partial pressure, laser frequency, and laser-output density, and substrate temperatures. Figure 3 is the one of the data for optimizing PLD deposition conditions. SZYO films were deposited on SrRuO₃ with a different laser frequency with 0.53 J/cm² of laser power density at 400 °C of the substrate temperature. As can be seen in Figure 3, only 8 Hz of PLD laser frequency can produce the single phase of SZYO. At the other laser frequencies, the films showed SrY₂O₃ phase despite they possess stoichiometric composition of SZYO.

In the same manner, we examined deposition conditions of SZYO and LSCF and the optimized the conditions. The optimized conditions for SZYO were as follows: oxygen partial pressure of 50 mTorr, laser frequency of 8 Hz, laser-output density of 0.53 J/cm², and substrate temperature of 400 °C. On the other hand, the optimized deposition conditions for LSCF were oxygen partial pressure of 50 mTorr, laser frequency of 4 Hz, laser-output density of 0.53 J/cm², and substrate temperature of 650 °C.

3.3 Proton conductivity of PLD deposited SZYO
Proton conductivity of SZYO deposited on Pt/SiO₂/Si substrate by the PLD method was evaluated in dry and wet Ar atmospheres in comparison with the sputtered SZYO reported by M. Arab Pour Yazd et al. [4] (Figure 4).
The conductivity of derived SZYO is smaller than that of the sputtered one; however, the activation energy in dry atmosphere is almost comparable. We need more improvements of the proton conductivity to achieve better SOFC property.

3.4 Cell performance at intermediate temperatures

Figure 5 is the current density-output voltage and current density-power density characteristics of the SOFC cell operated at 400 and 450 °C. We have successfully obtained power generating characteristics as low as 400 °C. However, its maximum power densities were about 1.2 and 2.4 mW/cm² at 400 and 450 °C, respectively, which are two decade smaller than that of commercialized SOFCs. The origin of the low power density might be the cathode of LSCF. As the LSCF later was deposited by the PLD method, the deposited LSCF film was solid and has no pores. This means oxygen (O₂) can be supplied only by the diffusion of the O₂ ions through the LSFC layer. The insufficient supply of the O₂ brings suppressing a reaction between H₂ and O₂, which results in less power generation.

In general, porous cathode was generally used in the conventional SOFCs to avoid this issue. However, the processing temperature of fabricating the conventional cathode is above 1000 °C, which is too high for our substrate. We are trying to fabricate porous cathode with a lower processing temperatures to obtain better SOFC operations.

4. Conclusion

We successfully demonstrated low temperature operations at 400 and 450 °C. The SOFC was fabricated on porous stainless steel substrate with Pd, SZYO, and LSCF as an anode, a proton conductive electrolyte, and a cathode, respectively. A solid Pd layer was fabricated on a porous stainless steel substrate by plating. Solid SZYO and LSCF films were deposited on the Pd-plated substrate by the PLD method. The substrate has good H₂ permeability at 300 and 400 °C; however it degraded at above 500 °C.

The fabricated SOFC cell showed low temperature operations at 400 and 450 °C. The power generation densities of the cell was 1.2 and 2.4 mW/cm² at 400 and 450 °C, respectively, which is two decades smaller than that of the conventional SOFCs. We consider the origin of this low power generation is insufficient O₂ supply through the cathode.

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