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Electrochemical analysis for anode-supported microtubular solid oxide fuel cells in partial reducing and oxidizing conditions

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ABSTRACT

Microtubular solid oxide fuel cells (SOFCs) with a diameter on the millimeter scale are suitable for small-scale applications such as micro combined heat/power systems and portable power sources. However, the use in reducing purge gas is not practical during start-up and shutdown in the small-scale applications. In this study, the redox tolerance was evaluated for nickel gadolinia-doped ceria (Ni–GDC) anode-supported microtubular SOFCs with an open-end at fuel outlet, when the hydrogen fuel supply was stopped 8 times for 10 min/cycle at 615 °C. The open circuit voltage was unchanged, and the degradation of less than 3% was confirmed after 8 redox cycles. The Ni–GDC anode-supported microtubular SOFCs have redox tolerance at 615 °C. Each electrode polarization resistance can be separated by the distribution of relaxation times (DRT) analysis from the measurement of AC impedance between the anode and the cathode. While the anode activation polarization (10–100 Hz) was clarified to increase because of the decrease in the TPB length, the anode concentration polarization (<1 Hz) decreased by the change in pore distribution after redox cycles. The DRT analysis is one of the most effective methods to investigate the mechanism of electrode degradation for microtubular SOFCs.

1. Introduction

Solid oxide fuel cells (SOFCs) are operated at temperatures above 600 °C, which enable to generate power high-efficiently without expensive noble catalysts such as platinum. A cermet of nickel-oxide ionic conductor (*e.g.* yttria-stabilized zirconia (YSZ) and gadolinia-doped ceria (GDC)) is generally used as an anode of SOFCs. The nickel catalyst has high activity for electrochemical oxidation of hydrogen fuel. Recently, anode-supported SOFCs with a thin electrolyte are widely applied to reduce the electrical resistance for lower temperature operation. However, nickel is more easily oxidized at high oxygen partial pressure. It is well known that an anomalous dimensional expansion of the nickel-based anode substrate induced the breakage of an electrolyte thin-film during re-oxidation [1–6].

Microtubular SOFCs with a diameter on the millimeter scale has advantages for lower temperature operation and rapid start-up. Suzuki et al. [7] reported that the maximum power density per cathode area reached 1 W/cm^2 at a low operating temperature of 550 °C for the microtubular single cell with a diameter of 0.8 mm. Kendall et al. [8] and Yashiro et al. [9] demonstrated the rapid start-up for microtubular SOFCs using butane fuel. The microtubular SOFCs are expected to be realized to small-scale applications such as micro combined heat/power (CHP) systems and portable power sources. In particular, the Ni–GDC anode had high durability at low operating temperatures below 600 °C under direct butane utilization in microtubular SOFCs [10,11].

The microtubular SOFCs with an open-end are strong against thermal shock because of no constraint at fuel outlet. A thermally self-sustained operation is easily possible by burning unreacted fuel around the open-end at fuel outlet for small-scale SOFCs. The microtubular SOFCs can be started up and shut down rapidly, which is effective to prevent re-oxidation of nickel catalyst for microtubular SOFCs. However, the use in reducing purge gas is not practical during start-up and shutdown in small-scale applications. Therefore, the reduction–oxidation (redox) tolerance of nickel-based anodes is required to be improved for microtubular SOFCs. Dikwal et al. [12] confirmed the degradation of 0.3% per cycle at 800 °C during 52 redox cycles for a Ni–YSZ anode-supported microtubular SOFC. The correlation between microstructural and electrochemical characteristics during redox cycles at 1000 °C were previously evaluated by AC impedance measurements and microstructural observations with focused ion beam-scanning electron microscopy (FIB-SEM) for an electrolyte-supported planar SOFC [13]. The polarization resistance of Ni–YSZ anode increased with redox cycles because of the decrease in the length of triple phase boundary (TPB) among nickel, YSZ particles and pore. Unfortunately, it is difficult to analyze AC impedance spectra by a general method of complex non-linear least squares (CNLS) with equivalent circuit models, as several electrode processes generally overlap within the experimental impedance spectra measured between the anode and the cathode for microtubular SOFCs without reference electrode.

Previously, the authors were successful in separating the anode and cathode polarization resistances by the distribution of relaxation times

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(DRT) analysis for anode-supported microtubular SOFCs [14,15]. This method can directly detect the number of electrode processes using mathematical techniques without assuming the equivalent circuits for SOFCs [16,17]. In this study, the change in polarization resistance was evaluated by DRT analysis to investigate the degradation mechanism of the Ni–GDC anode in partial redox conditions for microtubular SOFCs with an open-end at fuel outlet.

2. Experimental

Anode microtubes were constructed from NiO (Sumitomo metal mining), $Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC; Shin-etsu Chemical), pore former (acrylic resin; Sekisui Plastic) and binder (Cellulose; Yuken Kogyo) powders. The weight ratio of NiO to GDC was 60:40, and the particle size of the pore former was *ca.* 5 μm. These powders were mixed with a kneading machine by adding an appropriate amount of water over a period of 2 h. The anode microtubes were extruded using a piston cylinder with a metal hold with an outside diameter of 2.4 mm and an inside diameter of 2.0 mm. After extrusion, the tubes were dried overnight in air at room temperature. A slurry was prepared by mixing 8YSZ, binder (polyvinyl butyral; Sekisui Chemical) dispersant (tallow propylene diamine, Kao) and plasticizer (dioctyl adipate; Wako Pure Chemical Industries) into ethanol and toluene solvents for 48 h. The 8YSZ electrolyte was formed by dip-coating. The 8YSZ thin-film electrolyte and the NiO–GDC anode microtube were co-sintered for 3 h in air at 1400 °C. The interlayer of GDC and the cathode of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF)–GDC (70:30 wt.%) were coated by a similar manner. The interlayer and cathode thin-film layers were sintered sequentially in air for 2 h at 1250 °C and for 1 h 950 °C, respectively. The microstructure was observed using a field emission-scanning electron microscope (FE-SEM; JEOL JSM-6330 F) with an accelerating voltage of 15 kV. The thicknesses of the anode, electrolyte, interlayer, and cathode were *ca.* 200, 5, 1, and 20 μm, respectively.

Fig. 1 shows the experimental setup for electrochemical evaluation of the anode-supported microtubular SOFC. The outside diameter of the microtube was 1.8 mm, and the length of cathode was 30 mm after sintering. One end of the cell was opened, and unreacted fuel burned around the fuel outlet. Silver wires were used as a current collector. The characteristics of power generation and AC impedance were evaluated with potentiostat/galvanostat build in impedance analyzer (Autolab PGSTAT302). Firstly, a galvanostatic measurement was conducted at 0.15 A/cm^2 and 615 °C for 16 h with a supply of 20%H_2–3%H_2O–77%N_2 fuel to the anode side, and with a supply of air to the cathode side. Secondly, air was aspirated naturally into the anode inside from the open-end at fuel outlet, while the fuel supply was stopped for 10 min. After the fuel of 20%H_2 was supplied to reduce Ni–GDC anode for 20 min, the current of 0.15 A/cm^2 was loaded for 20 min. Then, AC impedance was measured under OCV in the frequency range from 100 kHz to 0.1 Hz with 20 steps per logarithmic decade. One redox cycle was from the fuel stop to AC impedance measurement, and 8 redox cycles were conducted at 615 °C in this study. Current–voltage characteristics were evaluated from open circuit voltage (OCV) to 0.4 V at a sweep rate of 5 mV/s. The distribution function $g(f)$ was calculated using the software program FTIKREG [18] to solve an ill-posed inverse problem by Tikhonov regularization. The inductance components were removed by the same method as described in refs. [14,15] before DRT analysis for the impedance spectra.

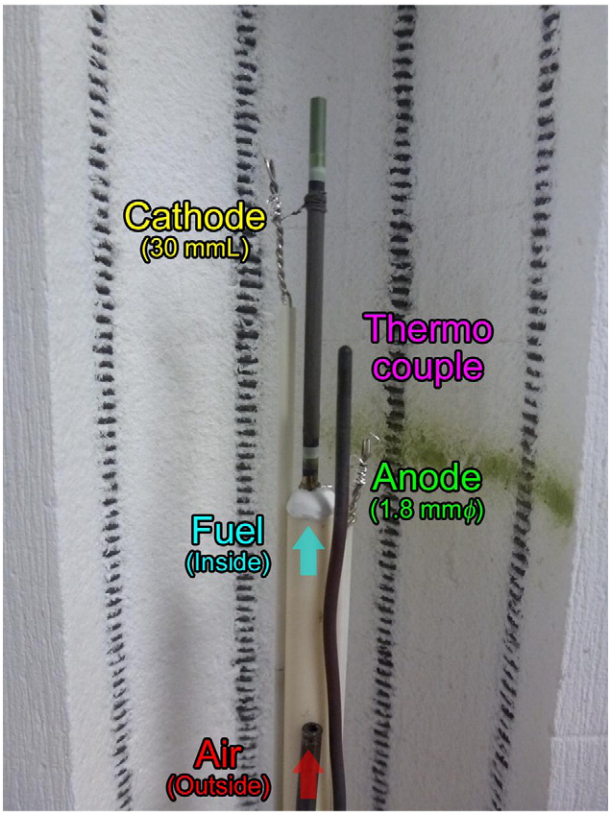

Fig. 1. Experimental setup for electrochemical evaluation of anode-supported microtubular SOFC.

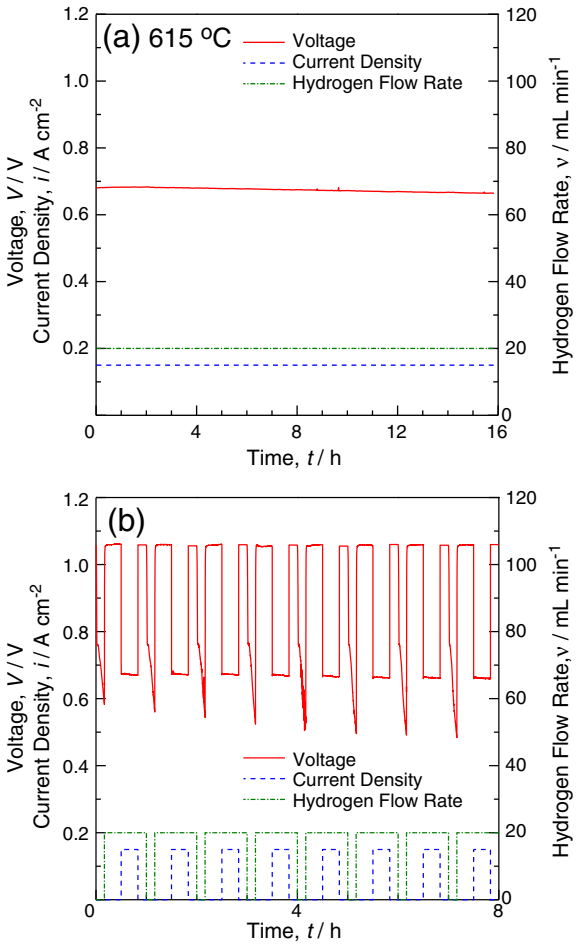

Fig. 2. Time courses of voltage, current density and hydrogen flow rate at 615 °C in (a) galvanostatic and (b) redox cycle conditions.