Short communication

Effects of anode microstructures on durability of microtubular solid oxide fuel cells during internal steam reforming of methane

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ABSTRACT

When hydrocarbons are used as a fuel in solid oxide fuel cells (SOFCs), internal steam reforming increases the energy conversion efficiency and simplifies the system, including the balance-of-plant. However, conventional nickel–yttria stabilized zirconia (Ni–YSZ) anodes are prone to deterioration at high temperatures and high humidity. This paper focuses on effects in anode microstructure on performance and durability of microtubular SOFCs. The evaluations were conducted under high steam content and internal methane reforming conditions using Ni–YSZ anodes using acrylic resin and graphite pore formers. The initial cell performance was almost identical to that of SOFCs with anodes using acrylic resin and graphite pore formers in 40% H_2–3% H_2O at 700 °C. However, the anode using acrylic resin deteriorated rapidly in 40% H_2–30% H_2O over a period of 28 h. Furthermore, it generated almost no electric power by internal steam reforming of methane. The local oxidation of nickel particles was observed at the interface between the electrolyte and the deteriorated anodes. The anode using graphite pore former provided stable power generation in 40% H_2–30% H_2O, and was able to generate power in 10% CH_4–30% H_2O. The pore formers strongly affect fuel diffusivity in the SOFC anodes, which is an important factor in stable internal steam reforming of methane.

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1. Introduction

Solid oxide fuel cells (SOFCs) can, in principle, directly use both hydrogen and hydrocarbon fuels such as methane, propane and butane. Many researchers have been successful with direct electrochemical oxidation of hydrocarbons on SOFCs [1–5]. However, hydrocarbons decompose into hydrogen and solid carbon at high temperatures [6]. As a result, carbon deposition causes rapid deterioration of the cells due to the deactivation of electrode catalysts and the inhibition of fuel diffusion. A steam/carbon (S/C) ratio of 2.5 or more is required in order to prevent carbon deposition in the external steam reforming of methane [7].

A cermet of nickel–yttria stabilized zirconia (Ni–YSZ) is widely used as an SOFC anode. Some researchers successfully demonstrated internal steam reforming of methane on SOFCs at S/C ≤2 [8,9]. However, Matsui et al. [10] reported that the performance of these anodes deteriorated rapidly for 69 h in a highly humidified hydrogen (70% H_2–30% H_2O) at 1000 °C. Hauch et al. [11] suggested that nickel can deform via the production of $Ni(OH)_2$ gas phase at high temperatures and high humidity. The internal reforming of highly humidified methane (S/C = 3) resulted in the gradual deterioration of the anodes due to decreasing methane conversion [12].

It is well known that the anode microstructure affects the electrochemical properties of SOFCs. A pore former is normally added to raw anode materials to increase porosity. After sintering, macropores in anodes arising from acrylic resin are identical in size to those arising from a pore former. The walls of the macropores were packed with nickel and YSZ particles, which decrease the maximum fuel utilization and inhibit diffusivity in dilute hydrogen fuel for anode-supported microtubular SOFCs [13]. On the other hand, graphite pore formers are capable of producing uniform micropores with a diameter of several hundred nanometers in the anodes. The anodes using a graphite pore former facilitated superior fuel utilization of 93% in 10% H_2–3% H_2O–87% N_2. The initial performance of the Ni–YSZ anode using a graphite pore former was the same as that using an acrylic resin pore former under low hydrogen fuel utilization. However, it is unclear how the anode microstructure affects the performance and durability in highly humidified methane. In this study, the characteristics of acrylic resin and graphite pore formers were evaluated in Ni–YSZ anode-supported microtubular SOFCs. In these experiments, a high steam content (30%) and an internal methane reforming condition (S/C = 3) were used.

2. Experimental

A composite anode of 60 wt.% NiO (Sumitomo Metal Mining)–40 wt.% $(Y_2O_3)_{0.08}(ZrO_2)_{0.92}$ (YSZ; Tosoh) was used in this study. A pore former of 10 wt.% acrylic resin (Sekisui Plastic MBX-5) or graphite

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(Showa Denko UF-G10) with a grain size of ca. 5 μm was added to the NiO–YSZ composite anode before sintering in order to increase porosity. The anode microtubes were extruded using a piston cylinder. The YSZ electrolyte slurry was dip-coated, and co-sintered in air with the NiO–YSZ anode microtube at 1400 °C for 3 h. Next, the interlayer of $Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC) and the cathode of 70 wt.% $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$– 30 wt.% GDC were dip-coated, and sintered sequentially in air at 1250 °C for 2 h and 950 °C for 1 h, respectively. The outside diameter of the microtubes was 1.8 mm and the length of the cathode was 10 mm after sintering. The thicknesses of the anode, electrolyte, interlayer and cathode were ca. 200, 5, 1 and 20 μm, respectively.

The characteristics of power generation and AC impedance were evaluated at 700 °C with a potentiostat/galvanostat and an impedance analyzer (Solartron Analytical 1470E/1455). The flow rates of fuel and air were set to 100 mL/min. First, a mixture of 40% H_2–3% H_2O–57% N_2 was supplied to the anode for 2 h at 700 °C for reduction treatment. The porosities of the reduced Ni–YSZ anodes using the acrylic resin and graphite pore formers were 41 and 36 vol.%, respectively [13]. After the initial electrochemical evaluation, the fuel was changed to 40% H_2–30% H_2O–30% N_2. Durability tests were conducted at a constant current density of 0.5 A/cm². For other samples, a similar sequence was conducted prior to the durability test. Next, the fuel was changed to 10% CH_4–30% H_2O–60% N_2 (S/C = 3), and an electrochemical evaluation and durability test at 0.5 A/cm² was conducted. After the durability test, the same fuel (40% H_2 or 10% CH_4–30% H_2O) was supplied to the anode as it cooled from 700 °C to room temperature over a period of 70 min in order to maintain the microstructure as possible. The anode microstructures were observed with a field emission-scanning electron microscope (FE-SEM; JEOL JSM-6330F) following the durability tests.

3. Results and discussion

Fig. 1 shows the AC impedance spectra at open circuit potential (OCP) and 0.5 A/cm². The impedance spectra were almost the same in 40%H_2–3%H_2O at 0.5 A/cm² and in 40% H_2–30% H_2O. However, cell performance decreased, when the fuel was changed from hydrogen to methane. The ohmic losses for the Ni–YSZ using graphite pore former in 40% H_2–30% H_2O and 10% CH_4–30% H_2O were 0.19 and 0.23 Ω cm², respectively. The decrease in cell temperature was estimated from the activation energy of ohmic loss [14] and found to be approximately 15 °C. This change in temperature was attributed to the endothermic reaction of the steam reforming of methane.

Fig. 2 shows the results of durability tests at 0.5 A/cm² in 40% H_2–30% H_2O and 10% CH_4–30% H_2O at 700 °C. The initial performance in CH_4 was lower than that in H_2 as shown in the inset on the left side of
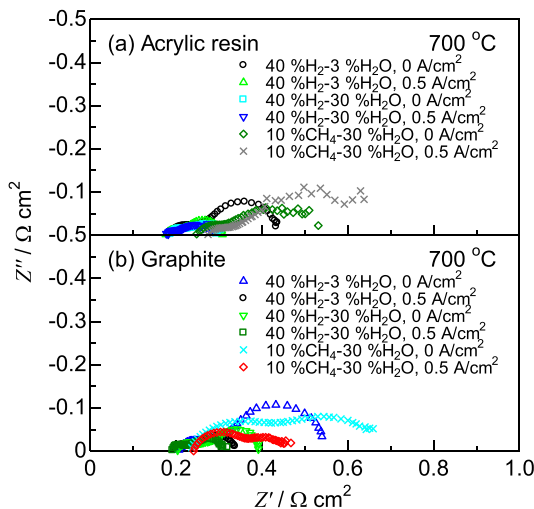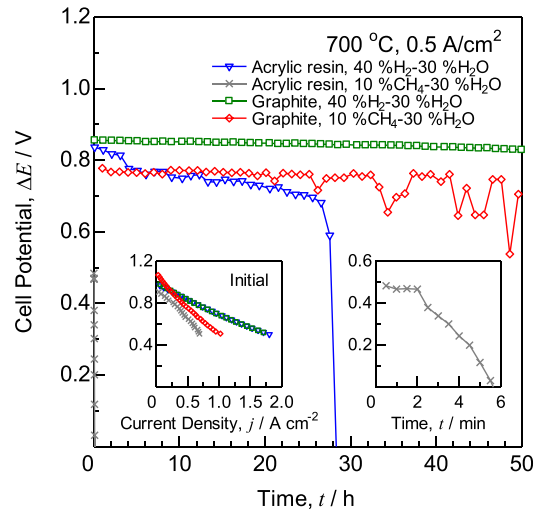
Fig. 2. Time courses of cell potential during durability test at 0.5 A/cm². The left-hand of inset is the initial cell potential-current density characteristics.

Fig. 2, because the polarization resistance increased due to internal steam reforming of methane. In the case of the acrylic resin pore former, the cell potential gradually decreased in 40% H_2–30% H_2O over the initial 28 h period. The polarization resistance increased, while the ohmic loss was unchanged (Fig. 3(a)). The cell potential dropped rapidly after 28 h in 40% H_2–30% H_2O for the acrylic resin pore former. Furthermore, the Ni–YSZ anode using the acrylic resin pore former performed poorly at
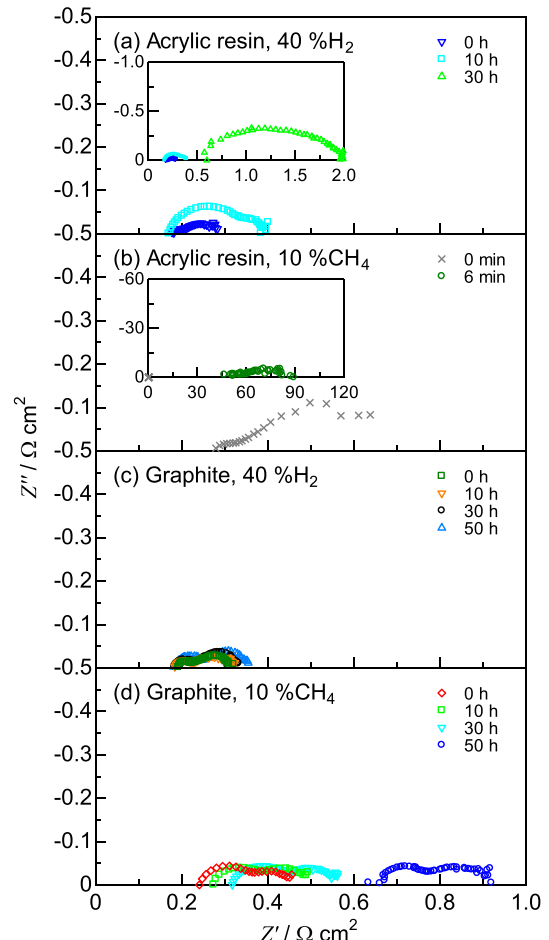
Fig. 1. AC impedance spectra at OCP and 0.5 A/cm².

Fig. 3. AC impedance spectra during durability test at 0.5 A/cm².