Structural investigation of electrochemically active ceramic anodes for next-generation solid oxide fuel cells (SOFCs) and solid oxide electrolysis cells (SOECs)

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Electrochemically active ceramic anodes for next-generation solid oxide fuel cells (SOFCs) were studied by controlling the anode structure at the submicro-scale. Specifically, the effect of highly porous metal-ceramic structures on electrochemical properties such as power density and conversion efficiency at an intermediate temperature was investigated. Moreover, the structural control technology of active fuel electrodes for direct hydrocarbon SOFCs was discussed. In addition, high-temperature steam solid oxide electrolysis cells (SOECs) with highly porous fuel electrodes have been developed for advanced ceramic reactors.

Key-words : Anode-supported SOFC, Direct hydrocarbon SOFC, Advanced ceramic reactor, Rapid start-up SOFC, Intermediate temperature, Ceramic microstructure

1. Introduction

Ceramic electrochemical reactors using ionic conductive oxide materials such as solid oxide fuel cells (SOFCs) are of great interest for improving the energy conversion efficiency from hydrogen and hydrocarbon fuels. In 2011, SOFC systems appeared in the Japanese market for stationary applications such as home co-generation systems. More than 100,000 units of 700 W-type stationary fuel cells have been installed in Japan, contributing to a reduction of carbon dioxide emissions by 1.3 ton or more per year.1) High expectations are placed on SOFC technology such as long-term trouble-free operations, robustness of operations with rapid start/stop cycles, and diversification of fuel cell applications in high-efficiency portable power generators. To implement these properties in next-generation SOFCs, optimization of nano- and microstructures in metal-ceramic electrodes is extremely important for improving power density and efficiency. Moreover, solid oxide electrolysis cells (SOECs) are SOFC-type ceramic electrochemical reactors, which provide highly efficient electrochemical conversion, for example, of water to hydrogen, using renewable electric power.

The structure of active SOEC electrode affects the electrochemical reaction rate in terms of conversion and degradation under high temperature and humidity conditions. A research and development project called “ceramic reactor development” was implemented in Japan for advanced ceramic technology (FY 2005–2009). New ceramic electrochemical reactors with high power density per volume, such as anode-supported microtubular and microhoneycomb SOFCs, were developed as part of an industry-academia-government collaboration. In particular, 200 W SOFC stacks (2 W/cm³ at 600°C) with rapid start/stop cycles were manufactured by accumulation of microtubular SOFCs with a diameter of 2 mmϕ.2) In this paper, the properties of the active anode of microtubular SOFC/SOEC systems are discussed.

2. Experimental procedures

In the design of intermediate-temperature (<600°C) ceramic electrochemical cells, the use of an electrode-supported cell with a thin and dense ionic conductive electrolyte layer and a suitable interconnector is important for reducing the total cell resistance. The support electrode usually consists of a Ni-based ionic conductive ceramic anode [e.g., yttria-stabilized zirconia (YSZ), gadolinium doped ceria (GDC), and scandia stabilized zirconia (ScSZ)] with controlled composition and porosity to achieve the required thermo-mechanical stability (stability under a stress of a few hundreds of MPa) under the operating temperature. The manufacture of electrochemical cells by a typical wet processing method is shown in Fig. 1.

The anode support was fabricated by extrusion of a mixture of commercial NiO and ScSZ (Sc6.0Ce0.01Zr0.89O2) powders, water, cellulose binder, pore former [e.g., graphite powder or poly methyl methacrylate (PMMA) beads], and mixture clay [with hardness of about 12 points, measured by a type A durometer (ISO 7619)], through dies of different shapes (e.g., tubular, planar, and honeycomb). After drying, the surface of the extruded anode supports was coated by dipping into an electrolyte slurry such as ScSZ,

Fig. 1. Ceramic process for the fabrication of microtubular SOFCs.
YSZ, or GDC dispersed in an organic solvent, and co-fired at 1200–1300°C for 1–2 h in air. The interlayer of GDC and the lanthanum strontium cobalt ferrite (LSCF, commercial La0.6Sr0.4-Co0.2Fe0.8O3) cathode layer was slurry-coated and sintered by a similar process.

The thickness and microstructure of the ceramic electrode (such as composition, porosity, and sintered grain size) were dependent on the ceramic processing conditions. The pore structure of the Ni-zirconia electrodes strongly affects the electrochemical properties of SOFCs and SOECs at an intermediate temperature. Current–voltage ($I–V$) and impedance measurements of the ceramic electrochemical reactor were carried out using a Solartron 1287 electrochemical interface and a Solartron 1255B frequency response analyzer using a wet H2 and/or butane gas flow (Toyo Technica Co., Japan) at 400–600°C. The developed anode-supported microtubular SOFC (Ni–ScSZ/ScSZ/GDC/LSCF: diameter 2 mmΦ, anode length 20 mm, effective surface area of the LSCF electrode about 62.8 mm²) is shown in Fig. 2(a).

3. Results and discussion

3.1 Effect of microstructural control of the active ceramic anode on the intermediate-temperature electrochemical performance of SOFCs

The cell stack (200 W-class stack/200 cm²-class) was constructed by accumulating single cells of 2 mmΦ [Fig. 2(b)]. The microscale cross-sectional SEM photograph of a single cell is shown in Fig. 3.

For example, a multilayered cell structure consisting of a ScSZ dense electrolyte layer with a thickness of about 8 μm, a 200 μm thick porous anode, and a 20 μm thick cathode showed good reproducibility. In general, under oxygen partial pressure at high temperatures, oxide-ion diffusion takes place smoothly. Oxygen capture from the atmosphere is the electrochemical rate-limiting step for the ionization at the cathode.

On the other hand, the anodic reaction resistance was negligible resulting in a decrease of the electrochemical reaction rate at an intermediate temperature: The relationship between the porosity of the Ni–ScSZ anode (prepared using PMMA polymer beads as a pore former at a sintering temperature of 1200–1300°C) and cell resistance using a wet H2 fuel gas flow rate of 50 cm³ min⁻¹ at 600°C is shown in Fig. 4.3

Anode porosity was found to affect the electrochemical properties; in particular, the power density of the SOFC was improved by decreasing the cell reaction resistance at the intermediate temperature of 600°C [Eqs. (1) and (2)].

Max. Power Density = $V^2/4R_{\text{cell}}$ (1)

$V$: Voltage [$V$], $R_{\text{cell}}$: Electrochemical cell resistance [Ohm cm²])

$R_{\text{cell}} = R_{\text{ohmic}} + R_{\text{reaction}}$ (2)

$R_{\text{ohmic}}$ [Ohm cm²]: total cell Ohmic resistance, $R_{\text{reaction}}$ [Ohm cm²]: Electrochemical reaction resistance of both anode and cathode.

At this intermediate temperature, the diffusion resistance of the anode plays a rate-determining role; however, increasing the Ni–ScSZ anode porosity from 37 to 54% resulted in a decrease in the electrochemical resistance to 1/30, thereby increasing the power output to 1 W/cm²/°C. Another important issue to be addressed is that anode porosity is affected by deterioration of the Ni catalyst because of volume expansion due to oxidation to NiO by water vapor. Ni–ScSZ anodes with same porosity and different gas distribution structure were fabricated using different pore formers (PMMA polymer beads or ragged graphite powder).

The dependence of the gas flow velocity of anodes with 43% porosity and different gas distribution structures on the air flow velocity at room temperature is shown in Fig. 5. The pressure loss decreased with increasing cumulative pore volume as shown in Fig. 6.

When graphite was used as a pore former, the anode showed good gas diffusion properties with a gas permeation resistance at high gas flow velocity 10 times lower as compared to the use of PMMA polymer beads. A power generation test was carried out in wet H2 gas atmosphere with a high humidity of 60% at 600°C. The cell with an anode having high gas permeation properties, prepared using graphite as a pore former, showed better power generation without voltage drop.

On the other hand, we confirmed the rapid destruction of cells having an anode with high gas permeation resistance, due to low gas and water vapor emissions. Electrochemical anodic reactions are dependent on the number of submicrometer-sized pores.
However, for Knudsen diffusion, a narrow pore size distribution of the anode results in high diffusion resistance. In contrast, a wide pore distribution with many submicrometer pores is effective in increasing the electrochemically active sites such as the three-phase boundary sites. The increased vapor emission rate under high fuel utilization conditions contributes to the degradation of the Ni catalyst.

Figure 7 shows the \( I-V \) curves and fuel utilization percentage of 12 tubular SOFC bundles (4 mm \( \Phi \) x 12 cells) at 630°C (measurement conditions: fuel: 3% humidified \( \text{H}_2 \) (20–100 cm\(^3\)/min) + \( \text{N}_2 \) (100 cm\(^3\)/min) or 3% humidified \( \text{H}_2 \) (500 cm\(^3\)/min) Air: 300 cm\(^3\)/min).

3.2 Multi-fuel capability of microtubular SOFCs

SOFCs have the advantage of multi-fuel capability based on the reaction of oxide ions without the need for pure hydrogen; for example, domestic fuels such as city gas and liquid petroleum gas (LPG) can be used. However, when using dry hydrocarbon fuels, carbon deposition on a SOFC anode is thermodynamically favorable at low temperatures, and increases with decreasing operating temperature. Moreover, small transition metals, such as Ni, in anodes increase the rate of catalytic carbon deposition.

The use of direct hydrocarbon fuels at low temperatures is an important strategy for the simplification of SOFC systems, which allow rapid start-up from room temperature. Direct hydrocarbon SOFCs were demonstrated to improve the anode catalytic activity by preventing carbon deposition under reducing atmosphere. Cerium oxide (ceria) has catalytic oxidative properties related to the presence of oxygen vacancies, and is used for hydrocarbon combustion in automobile exhaust gas below 500°C.

On the basis of these properties, ceria has also been used in direct hydrocarbon SOFCs. Pure ceria catalyst has low ionic conductivity, and composite anodes show high electrochemical resistance at an intermediate temperature. Carbon deposition was successfully minimized without decrease in cell resistance by coating a ceria functional layer on the inner surface of the anode tube of a SOFC for direct methane fuel at 450°C. In addition, we developed an anode for LPG fuel reforming at an operating temperature below 600°C. For direct LPG fuel utilization, a highly porous GDC (Gd\(_{0.2}\)Ce\(_{0.8}\)O\(_2\)) anode-supported SOFC was developed by our ceramic structure-controlling process.
In this work, we report on the development of an active anode for ceramic electrochemical reactors with pore microstructure control, and a stack manufacturing process from single cells.

Next, the anode performance was demonstrated in a practical cell at an intermediate temperature. The effect of the ceramic electrode structure at the nanoscale level on the electrochemically active interface has also been investigated. The structural stability of the nanograins under the operating conditions is important to improve the electrochemical performance. A high SOFC/SOEC active area is a crucial parameter for reducing global carbon dioxide emission. Thus, the use of ceramic electrodes is expected to be a key technology for electrochemically active interfaces.

To meet the demand for future energy systems, our efforts will be directed toward the research of new ceramic manufacturing techniques for high-performance electrochemical devices.

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3.3 Development of functional electrodes for electrolytic cells

The demand for new energy carriers has encouraged the development of high-efficiency electrolysis systems for hydrogen production. Methane production from CO2 and hydrogen for urban gas via power-to-gas technology has been attracting great interest in Europe. A highly porous anode with 54 vol % porosity was prepared by our ceramic microstructure-controlling process under high steam and high current density at 700–800°C.

Figure 9 shows the cross section of the developed SOEC cell (Ni–YSZ/YSZ/GDC/LSCF–GDC; the effective reaction area is about 0.5 cm²). The thicknesses of dense electrolyte, Ni–YSZ anode, and LSCF–GDC cathode layers were about 5, 550, and 20 μm, respectively. A uniform pore size distribution was observed in the anode. An ideal gas permeation structure was achieved for high steam utilization.

The I–V curve for the developed SOEC with a highly porous Ni–YSZ anode measured at 700–800°C using 20% wet H2 (at a feed rate of 100 standard temperature and pressure cm³/min, passed through a water bubbler) is shown in Fig. 10. At the thermoneutral voltage, the current density was about 1.4 A/cm² at 800°C. Moreover, at a high steam utilization of 90% and residual water partial pressure of 0.02 MPa, the SOEC enables a stable electrolytic reaction at 800°C for 1 h even at a high current density of about 1.3 A/cm².

Our current efforts are directed toward the development of a new intermediate-temperature SOEC for methane production from carbon dioxide and steam (H2O) with co-electrolysis.

4. Summary

In this work, we report on the development of an active anode for ceramic electrochemical reactors with pore microstructure control, and a stack manufacturing process from single cells.