1. Introduction

Solid oxide fuel cells (SOFCs) have advantageous features such as multi-fuel capability and high conversion efficiency for co-generation and hybrid systems with heat engines. The high operating temperature allows the supply of heat and unburnt fuel to gas turbines, resulting in the highest efficiency among generation systems based on fossil fuels. The triple combined system consisting of SOFC, gas turbine, and steam turbine has been considered for application to natural gas and gasified coal fueled systems. In principle, internal reforming of the fuel could lead to high conversion efficiency, because thermal energy emitted by the electrochemical reaction can be chemically recovered by the endothermic steam reforming reaction. The deposition rates were significantly affected by types of metal and oxide in the cermet material and were related to the ionic/electronic conductivities of oxides and dissolution of carbon in the metal species. Extensive dilution of hydrocarbon fuel with water may lead to extremely high water concentrations in the downstream region of the fuel cell under discharge condition. High water content damages the Ni surface and catalytic activity by strong adsorption of water. Reconstruction and analyses of three-dimensional microstructures by focused ion beam-scanning electron microscopy were effective to clarify the degradation of the fuel electrode.

Keywords
Solid oxide fuel cell, Ni-YSZ cermet, Internal reforming, Carbon deposition, Microstructure, Degradation

Preliminary investigations for IGFC have assessed the tolerance of SOFCs for CO rich fuel with various undesirable minority components which are present in gasified coal fuel.

Yttria-stabilized zirconia is the most common electrolyte material for SOFCs, but requires an operation temperature of 750-900 °C because of the low ionic conductivity at low temperatures. Lower temperature operation of SOFCs is important to allow easy start-up and shut-down and gas sealing. Thermal degradation such as sintering and solid state reactions will also be minimized by lower temperature operation. Therefore, electrolyte materials with high ionic conductivities must be developed for SOFC operation at 700-800 °C. On the other hand, high temperature operation has advantages for high fuel flexibility and high efficiency. The ideal efficiency of the fuel cell, given by the Gibbs efficiency $\Delta G/\Delta H$, decreases with higher temperature, whereas actual efficiency is high for fuel cells operating at high temperatures due to the utilization of thermal energy and reduced overvoltages.

This paper summarizes the current status of the development of component materials for SOFCs. Further development of the systems include improved fuel electrodes and multi-fuel capability.
2. Component Materials for SOFC

The operation temperature for the SOFC stacks was set at about 1000 °C during the initial stage of the development. However, recent SOFC systems generally operate at 750-900 °C. Such lower temperature operation of SOFCs has been investigated actively especially for small scale applications to one or a few kW-class modules. Thermal degradation due to thermal expansion mismatch, solid state reaction between components, and sintering can be avoided by operating the cells at 700-800 °C without affecting the excellent flexibility for various fuels. Lower temperature operation also enables the use of metallic components and glass-based sealants. Three approaches have been used to enable low temperature applications, a thinner electrolyte layer, highly active electrodes and electrolytes with high conductivity. Substitutes for yttria-stabilized zirconia (YSZ) include scandia-stabilized zirconia (ScSZ), samaria-doped ceria (SDC), and lanthanum gallate. These electrolytes have higher ionic conductivities than YSZ, but each electrolyte still has disadvantages to be solved before practical use.

Two cathode materials are the most common in recent cells depending on the operation temperature. La$_{1-x}$Sr$_x$Co$_{1-y}$Fe$_y$O$_3$ (LSCF) perovskite is used in the temperature range of 700-800 °C whereas La$_{1-x}$Sr$_x$MnO$_3$ (LSM) is used in the range of 800-900 °C. LSCF is more reactive to electrolyte materials and has higher thermal expansion than LSM. Therefore, LSCF has higher activity for the cathodic reaction which is suitable for low and medium temperature applications.

Ni-YSZ cermet is most common as the fuel electrode (anode). The mixture of Ni and YSZ is used for enlargement of the triple phase boundary, stabilization of the microstructure, strong bonding, and minimization of thermal expansion mismatch to YSZ. The anode is also being used as the support material for the cell to attain sufficient mechanical strength of the cells. The following part of this article discusses the anodic reaction and fuel flexibility of the SOFC.

3. Fuel Flexibility of SOFC and Internal Reforming Processes

Hydrocarbon fuels are the most suitable for SOFCs to achieve high electrical efficiency from fuel resources. Three types of hydrocarbon fuel conversion methods can be considered for the combination of SOFC and reforming reaction as shown in Fig. 1. External reforming operation (a) converts hydrocarbon in the reformer prior to introduction to the fuel cell chamber. Such fuel processing is the only possible method for combination with low temperature fuel cells because of the high temperature required by the reforming reaction (ca. 700 °C). Indirect internal reforming (b) requires that the catalytic reformer is located inside the fuel cell chamber, so the reforming reaction is carried out in the vicinity of the cell stack. Direct internal reforming (c) directly introduces natural gas or hydrocarbon fuel to the cell chamber where the hydrocarbon is converted into hydrogen and carbon monoxide on the cermet anode. The Ni-YSZ anode is active for this reforming reaction.

Most systems adopt a combination of indirect-direct internal reforming, in which the small pre-reformer is

![Diagram of three modes of operation: (a) External reforming, (b) Indirect internal reforming, and (c) Direct internal reforming.](image)

Fig. 1 Three Modes of Operation of Fuel Cells with Reforming Reaction
installed in the fuel cell chamber to recover the heat generated by the electrochemical reaction for endothermic reforming. In many cases, reforming is completed on the anode surface. Conversion of natural gas to a methane and hydrogen mixture is necessary for the pre-reformer unlike the general reformer for complete hydrogen production (Fig. 2). Ethane and higher hydrocarbons should be completely decomposed by the pre-reformer to avoid carbon deposition in the stack.

The reactions proceed on the fuel electrode is shown in Fig. 2. The steam reforming of methane (1) and the water gas shift reaction (3) are considered. In addition to these reactions, dry reforming (reaction (2)) proceeds as carbon dioxide is formed by the electrochemical oxidation of CO and the shift reaction. Generally, the Ni catalyst is sufficiently active in the temperature range above 650 °C. The conversion is further limited by the equilibrium. Since the reforming reaction is highly endothermic, the equilibrium conversion increases as the reaction temperature rises up to almost 100% at 700 °C or higher. Hydrocarbon fuels should be supplied with caution to avoid carbon deposition. Carbon deposition occurs either through the cracking reaction (4) at 600-700 °C or by the equilibration of disproportionation of CO (Boudouard reaction (5)) below this temperature range. The deposited carbon covers the Ni surface in the initial stage, and finally results in pore closure and blocking of access of the gaseous reactants to the reaction sites. Adequate steam should be added to the hydrocarbon fuel to prevent carbon deposition. The oxidant CO2 and H2O are also formed by anodic electrochemical oxidation at the triple phase boundary (TPB). Therefore, carbon deposition significantly proceeds in the open circuit condition, since no electrochemical formation of water occurs4. The triple phase boundary in the Ni–YSZ system is defined as the boundary between Ni, YSZ, and the gas phases.

Commercial household SOFC units are equipped with a steam reformer for production of hydrogen and carbon monoxide from methane. Exothermic heat is supplied from an SOFC generator unit to the endothermic reforming reaction for increased fuel energy. The gains of total and electrochemical energies before and after reforming of methane at 800 °C are shown in Fig. 3. The total energy gain with reforming is equal to the endothermic heat supplied from the environment. The maximum electrical energy corresponds to ∆G of the combustion of methane and reformate. The thermal energy is further divided into usable and unusable energies defined as high (800 °C) and low (25 °C) temperature heat sources. A large amount of unreformed methane is not directly supplied to the fuel cell unit to avoid rapid progress of the endothermic reaction and the consequent temperature decrease, whereas methane can be partly supplied because of the adequate catalytic activity of Ni-based cermet for the reforming reaction. Even with direct supply of methane, methane is not oxidized directly by the electrochemical reaction. Instead the combination of thermal catalytic reforming and electrochemical oxidation of hydrogen and carbon monoxide proceeds on the Ni surface and triple phase boundary, respectively. If a non-equilibrium gaseous mixture of CH4, H2, CO, H2O, and CO2 is supplied to the SOFC cell, the open circuit voltage is determined by the equilibrium of H2, CO, H2O, and CO2. Methane acts as inert gas for determining the open circuit voltage.

Fig. 2 Electrochemical and Chemical Reactions in the Vicinity of the Triple Phase Boundary (TPB) of the Fuel Electrode

Fig. 3 Ideal Energy Obtained from Methane, Reformed Gas, and Partial Oxidation Reformate at 800 °C
4. Carbon Deposition

Direct supply of methane is worth investigating not only for simplification of the fuel supply system, but also for clarification of the effect of accidental supply of concentrated methane. Thermal and catalytic cracking of hydrocarbons should be avoided as the reaction results in carbon deposition. The equilibrium region of carbon deposition is shown in the C-H-O diagram of Fig. 4. At high temperatures above 800 °C, the straight line connecting carbon monoxide and hydrogen is the boundary of the carbon deposition region. For the reforming system of mixed methane and water, the steam to carbon ratio (S/C) of unity is the boundary of the carbon deposition region. At lower temperatures, disproportionation of CO and methane formation becomes favorable which corresponds to the bending of the carbon deposition region. However, carbon deposition proceeds even outside this region, especially in the presence of C2 and higher hydrocarbons. Carbon deposition becomes serious with higher carbon number of the fuel because of carbon residue.

The current versus voltage characteristics were measured before and after direct supply of C3H8. The steam to carbon ratio was set outside the deposition region estimated from the thermodynamic characteristics, and the terminal voltage was significantly lowered after generation with C3H8 (S/C = 3.0) (Fig. 5). Carbon deposition proceeded on the Ni cermet electrode, especially in the open circuit condition. Direct introduction of higher hydrocarbons has been suggested but at the operating temperatures of SOFCs, hydrocarbon fuels are converted nonselectively to carbonaceous species and solid carbon by cracking. Both cracking to lower hydrocarbons and chain growth to carbonaceous deposits occur. Thus, the high activity for reforming is important to avoid nonselective side reactions. The general countermeasure to suppress deposition of carbon is to supply excess water. Steam is supplied as part of the feed gas, but the fuel electrode is protected by steam and CO2 formed by the electrochemical reaction. The ease of carbon deposition on the electrode is dependent on the cermet material as well as the S/C ratio. Therefore, another approach to avoid carbon deposition is to design catalysts which are less active for carbon formation. The fuel electrode catalyst should be designed to achieve high electrocatalytic activity in addition to reforming activity and suppression of carbon deposition. The deposition rate is significantly affected by the types of metal and oxide in the cermet material as demonstrated by the gravimetric measurement of deposited carbon in Fig. 6. Metallic nickel demonstrated high activity for carbon deposition, whereas Ru-cermet resulted in hardly observable carbon deposition. Based on the gravimetric analysis, the relative deposition rates of carbon for Ni- and Ru-based cermets were:

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Fig. 4 Equilibrium Carbon Deposition Region in the C-H-O Diagram

Fig. 5 I-V Characteristics for a Ni-YSZ Anode Cell with H2 Supply Bubbled at 0 °C before and after Generation with C3H8 (S/C = 3.0)

Fig. 6 Gravimetric Measurement of Carbon Deposition on Various Ni- and Ru-cermets Using CH4 (S/C = 0.0027) at 1000 °C
The low deposition rate for the Ru-based cermet was attributed to the lower solubility of carbon in the metallic bulk than for the Ni-based cermet. Ru is more active for the steam reforming of hydrocarbon than nickel, but the high cost of this compound is a drawback to practical application. Fabrication of cermet with good contact with the electrolyte is also difficult due to evaporation of oxide in an oxidizing atmosphere and poor sinterability in a reducing atmosphere.

Copper has been proposed as a cermet component to avoid carbon deposition\(^{10}\). However, copper metal undergoes rapid sintering at 700 °C or higher. The small amount of carbon deposition for Ni-ScSZ may result from its high ionic conductivity. SDC possesses only poor ionic conductivity under severe reducing conditions of carbon deposition. However, Ni demonstrated high activity for gasification of deposited carbon. Some less active oxide anodes have been proposed. However, cracking of hydrocarbon at elevated temperatures should be considered.

The deposited carbon was characterized by micro-Raman spectroscopy as shown in Fig. 7. Two types of deposited carbon were observed, graphitic carbon deposited on the surface of the Ni metal at the initial stage of deposition, and a large amount of amorphous carbon deposited on the outer surface and in the pores of the fuel electrode layer\(^{11}\). Amorphous and graphitic carbons were observed at 1350 cm\(^{-1}\) and 1585 cm\(^{-1}\), which are expressed as the D- and G-band, respectively. The fuel mixture with S/C=1 led to slow deposition of graphitic carbon. The production of oxidants, CO\(_2\) and H\(_2\)O, with electrochemical oxidation of fuel restricted carbon deposition because of the enhanced oxygen potential in the vicinity of TPB. In contrast, low S/C at the open circuit condition led to rapid deposition of amorphous carbon. The graphitic carbon deposited on the surface could be easily removed by H\(_2\), H\(_2\)O or anodic oxidation current due to gasification. The large amount of amorphous carbon formed in the bulk Ni-YSZ cermet resulted in fatal and irreversible degradation of the cell.

One of the most important applications of SOFC systems is combination with coal gasification. Gasified coal gas is cleaned and supplied to the SOFC generation unit. Then the outlet gas with high thermal energy is introduced to a gas turbine generator. For this purpose, the degradation of the cells and stacks caused by the various contaminants in gasified fuel must be clarified. A number of contaminants such as sulfur, chlorine, COS, ammonia, and heavy metals can be expected even after cleaning of coal gas. For wider application of SOFC systems, other fuels such as liquid fuels, biofuels, dimethyl ether, or organic compounds in waste should be investigated.

5. Deterioration with Steam

Dilution of fuel with water is effective to avoid carbon deposition during the internal reforming process as well as in the reformate fuel supply. However, highly concentrated steam often leads to extremely high water content in the downstream region of the fuel cell after discharge of the cell because of the additional evolution of water by the electrochemical oxidation of hydrogen. Such extremely high water content deteriorates the active Ni surface and catalytic activity due to the strong adsorption of water\(^{21}\). The degradation of the anode proceeds under the discharge condition at low terminal voltage using fuel diluted with a large amount of steam. As shown in Fig. 8, the terminal voltage was stable at current density of 100 mA cm\(^{-2}\) even with high steam content, whereas gradual degradation was followed by a sharp drop of the terminal voltage at 200 mA cm\(^{-2}\). The amount of formed water was doubled by increasing the current from 100 to 200 mA cm\(^{-2}\). The deterioration with water was reversible in the initial stage at high terminal voltage, which was observable as a gradual degradation in terminal voltage. The high overvoltage became irreversible accompanied by a sharp drop in the subsequent degradation stage. High local water content in the vicinity of TPB facilitates strong adsorption on Ni.

Such degradation with steam is characterized by a large increase in ohmic resistance. Further deteriora-
tion is accompanied by both ohmic and polarization resistances, indicating that the conduction path was interrupted on exposure to concentrated steam. The initial performance of the fuel electrode after steam degradation was partly restored by reduction with dry hydrogen.

6. Microstructures of Fuel Electrodes after Degradation

Fuel cells are operated at high fuel utilizations, so the downstream part of the cermet anode is subjected to severe conditions due to the depletion of fuel and high steam concentration. Under such conditions, the oxidation and agglomeration of nickel proceed during long-term operation, leading to performance deterioration. As mentioned above, the microstructures of the electrodes significantly contribute to the performance and stability of SOFCs. Recently, direct observation of the electrode in a three dimensional (3D) space using focused ion beam-scanning electron microscopy (FIB-SEM) has become a powerful technique for microstructure analysis. FIB-SEM can provide essential information to understand the quantitative relationships between the microstructure, performance, and long-term stability. In this study, the microstructural changes in cell components with operating time were quantified by the FIB-SEM technique to elucidate the degradation of the fuel electrode under various operating conditions and atmospheres.

The performance stability of electrolyte-supported cell (Ni–YSZ | YSZ | LSM) was examined at 1000 °C by feeding humidified hydrogen fuel. The degradation behavior was significantly dependent on long term operation. The three dimensional microstructures of the Ni–YSZ are shown in Fig. 9. Hundreds of SEM images were obtained during ion etching-observation cycles of the topmost layers. From the stored SEM images, the virtual 3D microstructure of the fuel electrode was reconstructed by computer recognition of contrasts from the respective phases (YSZ, Ni, and pores). The triple phase boundaries of YSZ/Ni/pores extracted from the 3D image represent the electrochemical reaction sites which are illustrated as spatially expanded curves (Fig. 10). The density of TPB is directly connected with the electrochemical activity and decreases with sintering of Ni after long term operation. Nickel in the fuel electrode catalyst acts as an electrocatalyst for fuel oxidation, but also as a current collector forming a percolation network. The long term operation of the cell also resulted in interruption of Ni connections and Ni isolation as a result of sintering. The isolated Ni phase was easily recognized by the 3D image processing.

The 3-dimensional microstructure was observed for practical cells after long term operation. Sintering of Ni in the anode cermet was identified as one of the causes of degradation. The cell performance and degradation were well correlated with the TPB length in
the anode. The percolation of Ni grains in the cermet is essential for the electrical connectivity. The fraction of isolated Ni grains, which were not connected electrically with the network of Ni, increased after long term operation because of grain growth and sintering.

7. Conclusions

Solid oxide fuel cells have been investigated and developed as power generation devices with high conversion efficiency and excellent fuel flexibility. The excellent compatibility with various fuels as well as lower operation temperatures will also open new application fields for SOFCs. Direct internal fuel reforming within SOFCs is an effective operation mode because of its simplified system, but carbon deposition can cause severe deterioration. The ease of carbon deposition during generation. However, deterioration of the anode occurs with strong adsorption of steam in the presence of excess water. Design of the anode material and the steam to carbon ratio (S/C ratio) is essential for the electrical connectivity. The fraction of Ni grains, which were not connected electrically with Ni, increased after long term operation because of grain growth and sintering.

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