ABSTRACT

To realize “efficient and flexible” solid oxide fuel cells which can be operated in a variety of fuels without a rigid control of water content for reforming, we focused on the investigation of materials and catalysts for SOFC fuel electrode, electrolyte, and reforming devices. In addition to the combination of conventional electrode/electrolyte such as nickel / yttria stabilized zirconia, a new type of mixed conducting anode material, calcium titanate, was tested to understand the issues to be solved for direct oxidation of fuel in SOFCs. The results of cell testing and electrochemical or catalytic measurement of anodes should be correlated with the fundamental oxygen and proton transport properties of the materials.

INTRODUCTION

Our investigation is aimed at developing an efficient and flexible solid oxide fuel cell (SOFC) system in a moderate size (kW) range. SOFCs have, in general, higher efficiency than other types of fuel cells or diesel engines, and also have higher flexibility for fuels. However, the efficiency and fuel flexibility depends on the size of the system. In 1 MW-class stationary power generation systems, high efficiency can be achieved by combined SOFC/gas turbine systems, in which various fuels can be utilized by pre-reforming of hydrocarbons to methane and subsequent internal reforming of methane to carbon monoxide and hydrogen. The endothermic heat needed in the reforming
process is supplied from the Joule process during the power generation. However in a small system, it is not easy to achieve the high efficiency and fuel flexibility at the same time. The energy consumed in the reforming process is rather large compared to the Joule heat, which makes the system unattractive from the viewpoint of efficiency.

Direct introduction-oxidation of fuel is one possibility which ideally would result in a very high efficiency (1). It is desired that the direct introduction be possible regardless of fuel types, with humidification at room temperature if necessary. To understand the practical issues to realize direct introduction of fuels, we have focused on the relation between the reforming and the anode reactions, and organized a research collaboration team named FLEXSYS which consists of IWE (University of Karlsruhe), Kyoto University, University of Oslo, and AIST. This collaboration is aimed at cell components materials and systematic characterization of cell performances to extract the most important factors and to demonstrate the technological feasibility of the efficient and flexible SOFC stacks. In addition to the conventional electrode/electrolyte system such as Ni-YSZ, or Ce(M)O₂, new combinations including mixed conducting electrode materials are examined.

RESEARCH ACTIVITY OF FLEXSYS TEAM

Cell Testing and Characterization

Based on the experience in the field of preparation and characterization of conventional and advanced SOFC-materials (all types of perovskite type oxides, cermet and composites), the main focus at IWE is the development of FLEXSYS single cells (10 to 100 cm² electrode area) based on advanced materials characterized and evaluated by the FLEXSYS collaboration. The electrochemical characterization of these FLEXSYS single cells will be performed under realistic operation conditions in modified single cell test benches (2). The influence of water vapour on the cathode performance and stability is one emphasis. Testing of fuel flexibility will be carried out using single cells with appropriate gas mixtures. The loss mechanisms in single cells will be investigated by in-situ impedance spectroscopy. The (electro-) catalytic properties of different anodes under operating conditions will be monitored by in-situ gas analysis. Post mortem analysis of the FLEXSYS single cells (optical, SEM, EDX, TEM and microprobe) will be carried out in cooperation with other groups, to determine degradation mechanisms. Modeling of cell properties including a prediction of the stability and performance at given operating parameters will be the basis for stack modeling and system analysis. System analysis will be carried out in cooperation with the group of AIST and Kyoto University to get information about the efficiency and performance as well as the stable range of operation of a FLEXSYS stack (3, 4).

Up to now, different Ni/YSZ cermet varying in Ni content and NiO/YSZ particle size ratio (PSR = d₅₀(NiO) / d₅₀(YSZ)) have been investigated to analyze the interactions between composition, microstructural properties, kinetics of oxidation and reduction and
thermal expansion coefficient (TEC) in the oxidized and reduced states. It was found that the TEC significantly depends on the microstructural properties of the cermet as shown in Figure 1 and can be adjusted by using an appropriate composition and a particle size ratio. The impact of the composition (Ni/YSZ-ratio) and the particle size distributions of the constituents on the thermal expansion coefficient of the cermet have also been investigated (5).

Figure 1. TEC of NiO/YSZ-cermets as a function of particle size ratio and NiO-amount. In the left graph, lines represent the theoretical behavior according to Thomas and Schapery.

The reaction process of the basic system Ni/NiO was compared with cermet bulk samples and the influence of NiO and YSZ particle sizes and sintering temperatures on kinetics and microstructure was studied using thermogravimetry and dilatometry. It was found that bulk samples sintered at temperatures below 1300°C can withstand redox cycles much better than those sintered at higher temperatures. Furthermore, it was found that by decreasing the NiO particle size and using a NiO/YSZ particle size ratio of approximately 3:2, a smaller length increase after re-oxidation is achieved (6).

In addition to Ni/YSZ cermets, other anode material compositions have been investigated (CuO/GCO/8YSZ). Mixed conducting oxides, which exhibit electronic conductivity at least in the reducing environment of the anode, were selected to increase the number of active reaction sites. Raw materials were purchased from different suppliers. The materials were characterized with respect to their microstructural properties, surface area (BET), particle size distribution and sintering behaviour. The morphology and particle size distribution have been modified by thermal treatment and milling.

Due to the fact that the electronic conductivity of mixed conducting oxides is not sufficient to use these materials as a current collector, several cermets with a highly conductive metallic phase have been developed. For this metallic phase, either materials with a high catalytic activity like Ni or with a low catalytic activity (Fe, Cu) can be chosen. Alloys are interesting candidates for this and will be evaluated. The next step will be the electrochemical characterization of these compositions and preparation of single cells.
State-of-the-art single cells with a conventional Ni/YSZ cermet anode operating with methane and CO/H₂ mixtures were characterized. The first topic was the performance and stability of the conventional anode at low steam to carbon ratios (S/C < 2) with high amounts of CO (up to 100%). It was found that the maximum cell performance is achieved at an S/C-ratio of about 0.5.

Next to methane, the oxidation of CO and CO/H₂ mixtures was investigated. It was found that oxidation of CO using a state-of-the-art Ni/YSZ-anode is possible. Single cells operated with gas mixtures containing 25% CO showed nearly the same performance as if they were operated with pure hydrogen. At high CO-ratios the cell performance decreased, but even at 100% CO an acceptable power density was achieved. With decreasing temperature, the power density of the cell decreased significantly. This could not be attributed to only an increased internal cell resistance due to the thermally activated transport- and electrochemical-processes. A comparison of the I/V-characteristics at 950°C using hydrogen as the fuel before and after operating on CO at different temperatures revealed that a significant impairment of the anode took place (7). Next, electrochemical investigations of the performance of state-of-the-art single cells operating with propane and butane will be carried out.

The influence of fuel utilization on the cell performance was investigated. At high fuel and air utilization, due to small gas flow rates, the cell performance was not affected by the fuel composition at all. The stability of Ni/YSZ-cermet anode operating on dry methane was tested for more than 1000 h at 950°C and a constant current density of 400 mA/cm² (Figure 3). During the first 500 h of operation the performance decreased with a degradation rate of about 70 mV/1000 h. Then an increase in performance could be observed. Microstructural analysis after operation revealed that this type of anode can not be used in a stack operating at low S/C-ratios for several 10,000 h.

The temperature distribution and local gas composition at the anode of a single cell were simulated with the help of computational fluid dynamic program, FLUENT. In a first
step, the geometrical arrangement of the fuel supply for the single cell test benches was designed. An adaptation according to possible stack geometries is possible. Up to now, parameters for the state-of-the-art single cell have been used. Experimental data for reforming and electrochemical oxidation of the chosen fuel evaluated for different types of anode structures was incorporated to model the performance of advanced anode structures. This way, reforming and electrochemical oxidation of the fuel as well as the current density and temperature distribution within a cell could be calculated.

The results of the simulation will be compared with measured values of temperature distribution and gas composition analyzed by gas chromatography during operation of single cells. This tool will be helpful for the rating of different anode-structures and can also be used for the design of the stack by modifying the size of the single cell and the flow field.

![Image of a graph showing performance metrics for a fuel cell.]

**Figure 3.** Long-term stability of state-of-the-art single cell operated on pure methane (S/C = 0, fuel utilization: 25%).

Investigation on Electrode Materials and Reforming Catalysts

It has been found that a system that combines high transport of protons, oxygen ions, and electrons should be tested to realize the SOFC which works with direct introduction of fuels. In combination with the need to have a material compatible with present state-of-the-art components, we have chosen CaTiO₃ as one candidate which exhibits thermodynamic stability, suitable thermal expansion coefficient, and high proton mobility. Fe has been chosen as acceptor dopant, as it enhances both proton and oxygen vacancy concentration as well as electronic conduction. It has been checked experimentally that it does not react detrimentally with other anode components such as YSZ or Ni, while there may be a phase separation with segregation of some Fe under very reducing conditions. Tests of electrochemical property and catalytic activity were carried out.

**Preparation of Ni-Fe-CaTiO₃ Cermets and Power Generation Experiments:** NiO (Wako Pure Chemical Industries) and Fe-doped CaTiO₃ (Praxair) were used to prepare Ni-Fe-CaTiO₃ cermets in a disk electrode as follows. NiO and Fe-doped CaTiO₃ were
mixed in a weight ratio of 4:1. After the mixture was milled for 24 h, it was calcined at 1200°C for 5 h in air and then crushed into powder. This cermet powder was mixed with polyethylene glycol (Wako Pure Chemical Industries) to form slurry, and painted on one side of a YSZ disk of 8 mm in diameter and 0.2 mm in thickness. Then the disk was calcined at 1200, 1300, and 1400°C for 5 h in air. Ni-YSZ cermet calcined at 1400°C was also prepared as a reference. A perovskite-type La0.6Sr0.4MnO3 was prepared as follows: La, Sr, and Mn acetates (Wako Pure Chemical Industries) with the stoichiometric ratio were dissolved in water and then water was removed by heating the solution at 100°C and dried at 120°C. Resulting powders were milled for 24 h and calcined at 900°C for 10 h and subsequently mixed with polyethylene glycol to form slurry. This slurry was applied on the other side of the YSZ disk. The disk was calcined at 1150°C for 5 h in air. Prior to the power generation experiments, the anodes were reduced in a 50% H2/N2 stream from room temperature to 1000°C at a constant heating rate of 200°C/h. In power generation experiments, H2 humidified by bubbling at around 50°C or a gaseous mixture of 15% CH4, 45% H2O and 40% N2 was supplied as fuel gas to the cermets at 150 STP ml/min. Gaseous oxygen was fed to the La0.6Sr0.4MnO3 cathode, and current-voltage characteristics were measured at 1000°C on a Solartron 1287 potentiostat/galvanostat.

CH4 Steam Reforming over Fe-doped CaTiO3: Fe-doped CaTiO3 powder was pressed at 200kgf/cm², and then crushed and sieved into 0.6-1.7 mm. The sieved powders (1 mm³) were fixed in a quartz tube of 10 mm in diameter by packing quartz wool at both ends of the catalyst bed. Prior to the reaction, the catalyst was firstly reduced in a 50% H2/N2 stream from room temperature to 1000°C at a constant heating rate of 200°C/h. Then, a gas mixture composed of 14.4% CH4, 42.8% H2O and 42.8% N2 was fed at the total flow rate of 180 STP ml/min for steam reforming of methane over Fe-doped CaTiO3. Reaction products were analyzed by an on-line gas micro-chromatograph (Chrompack, Micro-GC CP2002). Catalytic activity was measured on decreasing reaction temperature from 1000 to 650°C.

RESULTS AND DISCUSSION

Figures 4(a) and 4(b) show the current-voltage characteristics at 1000°C for Ni-Fe-CaTiO3 cermets with H2 and CH4 as fuel, respectively. In the case of H2-fuel, current-voltage characteristics of SOFCs with the anode calcined at 1200 and 1400°C were significantly lower than that of calcined at 1300°C. The anode calcined at 1300°C exhibited a power generation performance comparable to that with Ni/YSZ cermet, though the difference in the voltage drop between the cermets gradually increased as the current density was raised. From visual observation, no apparent change was recognized for the cermet anodes calcined at 1200 and 1300°C in air for 5h, whereas the anode calcined at 1400°C turned to metallic at the surface. In the comparison of impedance spectra taken at OCV condition with 10-mV amplitude, a distinct change was observed in the right-most semicircle between the samples calcined at 1300 and 1400°C. It may be suggested from these results that during the calcination at 1400°C, the reactions between the anode components occurred and the anode structure was considerably altered, giving rise to the degradation in the power generation characteristics. Figure 4(b) shows the power generation characteristics of the SOFCs when CH4 is used as fuel. The Ni-Fe-CaTiO3 anode calcined at 1300°C demonstrated higher performance than the
anodes calcined at 1200 and 1400°C, as in the case of H2 fuel. The Ni/YSZ cermet exhibited still better power generation characteristics than the Ni-Fe-CaTiO3 anodes and the difference in the power generation characteristics between the Ni/YSZ and Ni-Fe-CaTiO3 anodes was larger in CH4-fueled SOFCs than in H2-fueled SOFCs.

Figure 5 shows methane conversion and CO, CO2, and H2 yield over Fe-doped CaTiO3 as a function of temperature. By the on-line analysis with a gas chromatograph, CO, CO2, and H2 were detected as the products during the CH4 steam-reforming reaction over Fe-doped CaTiO3. The catalytic activity of Fe-doped CaTiO3 was quite low: CH4 conversion increased gradually from 800°C, and even at 1000°C CH4 conversion remained at around 60%, although complete CH4 conversion can be expected thermodynamically at 750°C in the experimental conditions investigated (8).

Figure 4. Current-voltage characteristics of SOFCs with Ni-CaTi0.9Fe0.1Oxide and Ni-YSZ as anode at 1000°C: (a) H2-fueled, (b) CH4-fueled. Cell: Ni-CaTi0.9Fe0.1Oxide/YSZ/La0.6Sr0.4MnO3 or Ni-YSZ/YSZ/La0.6Sr0.4MnO3.

Figure 5. The profiles of CH4 conversion and CO, CO2, H2 yield for steam reforming reaction of CH4 over Fe-doped CaTiO3. Gas composition: 14.4% CH4, 42.8% H2O and 42.8% N2; Total flow rate, 180 STP ml/min.
Investigation of Oxygen and Proton Transport in Materials

FLEXSYS focuses on the investigations of defect chemistry and transport properties in oxide ceramics. It contributes to the understanding of how protons in or on oxide structures effectuate or affect the catalytic, charge transfer, and diffusion steps on SOFC anodes.

Figure 6. Schematic of mass spectrometer apparatus for isotope kinetics studies.

![Figure 6](image)

Figure 7. Oxygen isotope exchange on Sr-doped LaFeO₃ after inlet of a 1:1 mixture of ¹⁶O₂ and ¹⁸O₂ to a sample preheated in vacuum.

![Figure 7](image)

Figure 8. Hydrogen isotope exchange on Fe-doped TiO₂ after inlet of a H₂+D₂ mixture to a sample preheated in Fe-doped TiO₂ after inlet of a H₂+D₂ mixture to a sample preheated in vacuum.

![Figure 8](image)

The project has contributed to the development and construction of new apparatus for measurements of surface and bulk kinetics of hydrogen and other species based on isotope labeling and mass spectrometry. These results will be complementary to the electrochemical measurements. The first results are emerging for essential SOFC materials (YSZ, ceria, metals) and are being compared with results obtained through other related techniques (notably SIMS). It is hoped that these efforts will clarify some unresolved differences in the results in the literature regarding water and proton uptake in ceria, an issue considered important for the understanding and possible use of ceria as electrocatalyst in SOFC anodes. Figure 6 shows a schematic of the simple mass spectrometer apparatus referred to above, and Figs. 7 and 8 show examples that illustrate two of the types of experiments one may perform. In addition to deriving kinetics for simple dissociation reactions of oxygen and hydrogen as in these examples, it is of course essential to derive parameters for more complex reactions involving in particular water...
vapor and carbon containing molecules. Of these water vapor represents a particular challenge because of the operation of the mass spectrometer and parts of the vacuum chambers at temperatures relatively near its dew point.

Figure 9. Relative intensity of deuterium ion in YSZ and ScSZ specimens annealed in D₂O containing atmosphere.

Figure 10. Surface exchange rate constant (α) of ScSZ and Fe-ScSZ as functions of water partial pressure at T = 873 K. Solid line was derived from the concentration of water coverage on YSZ (eq. [1], Q_{ch,1} = 94 kJ/mol, Q_{ch,2} = 70 kJ/mol $K_t = 10^9 \text{ Pa}^{-1}$ from Ref. 10).

The effect of water vapor on oxygen exchange kinetics at the electrode or electrolyte surface have been also investigated by using isotope exchange experiments and subsequent secondary ion mass spectrometry (SIMS). The water solubilities of YSZ and scandium stabilized zirconia (ScSZ) were evaluated by annealing in D₂O containing atmosphere and subsequent intensity measurement of deuterium ion as shown in Figure 9. The relative intensity of $I_D/I_H$ detected in YSZ single crystal was on the order of $10^4$, which indicates that D₂O was hardly absorbed in YSZ lattice. However, all polycrystalline YSZ and ScSZ exhibited higher intensity ratio around $I_D/I_H = 10^3$, indicating that the D₂O component mainly absorbed in grain boundaries in polycrystalline.

Although the solubility of water in YSZ and ScSZ are very low, the surface exchange kinetics of oxygen atom on the surface of ScSZ and 3 mol % Fe doped ScSZ are affected by the existence of a slight amount of water vapor as show in Figure 10. Recently, we have found the quantitative relationship between the observed surface reaction rate and water coverage on the surface. The coverage of water molecule chemisorbed on YSZ surface ($\theta_{ch}$) is reported from Raz et al. (9) as a function of oxygen partial pressure ($P_{\text{H}_2\text{O}}$) and temperature (T) with assuming an equilibrium constant ($K_0$) and activation energy ($Q_{ch,1}$, $Q_{ch,2}$).

$$\theta_{ch} = \frac{1}{2} \left(\frac{1}{1 + P_{\text{H}_2\text{O}}^1 K_0^{-1} \exp(-Q_{ch,1}/kT)} + \frac{1}{1 + P_{\text{H}_2\text{O}}^1 K_0^{-2} \exp(-Q_{ch,2}/kT)}\right)$$  \[1\]
The solid line in Figure 10 represents the water vapor pressure dependence of $\theta_{\text{at}}$ at $T = 873K$, with reported values of activation energy ($Q_{\text{a,h}} = 94 \text{ kJ/mol}$, $Q_{\text{a,2}} = 70 \text{ kJ/mol}$) and an appropriate equilibrium constant ($K_0 = 10^{18} \text{ Pa}^{-1}$) (9). The line is in a good agreement with the experimentally obtained $p(\text{H}_2\text{O})$ dependence of surface reaction rate constant exhibiting a drastic increase in the lower $p(\text{H}_2\text{O})$ region and some saturation in higher $p(\text{H}_2\text{O})$ region. The increase of surface exchange rate may lead to the increase of interfacial conductivity in electrode/electrolyte interface, and it should be also investigated for the case of mixed conducting electrolyte and electrodes such as Fe-doped CaTiO$_3$.

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