DEVELOPMENT OF SOFC ANODES FOR INTERNAL REFORMING OF METHANE

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ABSTRACT

Today the SOFC based power generation systems of Siemens Westinghouse operate on natural gas, which is converted to hydrogen by reformer units, thermally integrated into the SOFC stack. One possibility to reduce the still high costs of these systems is to avoid the reformer units by running the reforming reaction directly on the anodes of the cells. But the Ni-YSZ-cermet anodes applied in the past catalyze the endothermic reforming reaction to such an extent that the cell is undesirably cooled down towards the fuel entrance. This may cause cell failure by thermomechanical stress and in addition the electrochemically active cell area and hence the efficiency are decreased. Therefore new cermet structures have been successfully developed which show reduced reforming activity whilst keeping the fast kinetics for electrochemical hydrogen oxidation of conventional cermets. This was achieved in two steps: by decreasing the porosity of the cermets and by applying NiCr alloys instead of Ni to further decrease the free Ni surface by formation of a chromium oxide scale on the metal particles.

INTRODUCTION

Natural gas fuelled power plants based on high temperature fuel cells (MCFC and SOFC) have been operated with system efficiencies which are far higher than those of low temperature systems (PEM, PAFC). This is due to the high operating temperatures which allow for driving the endothermic reforming of natural gas by the waste heat of the electrochemical oxidation of hydrogen (methane itself cannot be efficiently oxidized electrochemically). The effect on the electrical system efficiency is twofold. The fuel required for heating an external reformer is saved. The same holds for the electrical power necessary to withdraw this heat later on from the cell by a cooling cycle. Up to now the SOFC generators of Siemens use reformer units thermally integrated into the stack. A considerable cost of the still far too expensive SOFC systems is due to these reformer units. In principle it should be possible to eliminate these components by performing the reforming reaction directly on the anodes of the cells. The Ni-YSZ-cermets can act also as reforming catalysts but unfortunately they tend to speed up this reaction too fast. Thus due to its endothermic property the reforming reaction cools down the cell at the fuel entrance to an extent that cell failure by thermomechanical stress and
also a loss of active area for the electrochemical oxidation of hydrogen results. But new cermet structures should be able to avoid these problems if their performance could be tailored to meet certain target values which are derived in the next chapter.

DEVELOPMENT OF ANODES FOR INTERNAL REFORMATION

Experimental Methods of Characterization and Target Values

The methane turnover rate of the cermets was measured in the temperature range of 700 to 1000°C by exposing them to a mixture of methane and water vapor (S/C = 2). A small amount of hydrogen (2%) had further been added to this mixture to avoid oxidation and evaporation of Ni via volatile Ni hydroxide. This tends to happen at the fuel entrance where the gas mixture does not yet contain any trace of hydrogen so that oxidizing conditions prevail.

The cermet samples were prepared by screen-printing (printed area 4 or 16 cm²) and sintering onto a planar YSZ substrate sheet (25 cm²). This is a convenient way to prepare new electrode layers for testing purposes, even if they are later on applied to a different cell geometry like the tubular one.

The samples were then mounted into a cell housing made from alumina as commonly used for planar cell tests. The fuel flow being confined to a gap of 1 mm height above the cermet layer could be varied between 275 and 23 sccm/cm² related to the macroscopic surface of the cermet. Methane conversion was calculated from the change of gas composition between fuel inlet and outlet of the test cell as measured by a gas chromatograph.

A rate constant $k_{ref}$ for the reforming reaction was introduced by writing the turnover rate $r_{ref}$ of methane per macroscopic surface of the cermet layer (unit: mol/m²s) as

$$r_{ref} = k_{ref} * p_{CH4} * p_{H2O} (1 - Q_{ref}/K_{ref}) \quad [1]$$

where

$$Q_{ref} = \frac{p_{CO} * p_{H2}}{(p_{CH4} * p_{H2O})} \quad [2]$$

$K_{ref}$ is the equilibrium constant of the reforming reaction and the $p_i$ denote the partial pressures of the components of the fuel. A similar equation was used to characterize the shift reaction by a rate constant $k_{sh}$ and an equilibrium constant $K_{sh}$.

The methane turnover was found to be so high that it was not possible to consider it as differential. Therefore the rate equations had to be integrated numerically along the flow across the anode. $k_{ref}$ and $k_{sh}$ were adjusted so that the gas concentrations calculated for the cell exit agreed with the measured data.

The simple rate approach [1] was confirmed by varying the exponents of the partial pressures and comparing the results of the calculations with experimental data.
A target value for $k_{\text{ref}}$ can be derived by stating, that methane should be converted by the cermet at a rate which is equivalent to 0.5 A/cm$^2$, the typical electrochemical load current density at 950°C. Assuming further-on atmospheric pressure and S/C = 2 this implies $k_{\text{ref}} = 3 \times 10^{12}$ mol/(m$^2$sPa$^2$).

According to the described method of characterization, Ni-YSZ cermet anodes applied by Siemens so far yield values of $k_{\text{ref}}$ which are two orders of magnitude too large.

On the other hand, their impedance corresponding to the electrochemical oxidation of hydrogen is about 0.10 $\Omega$cm$^2$ when measured under a mixture of 50% hydrogen and 50% water vapour at 950°C (the mentioned gas mixture is suitable to model the situation of partially spent fuel in a stack). This value of impedance should not be surpassed by any future modification of the anode cerments.

### Sample Preparation

To achieve an inhibition of the reforming kinetics the porosity of the cerments was reduced in a first step. Conventional cerments show a porosity scattering in the range of 50 to 65%. Aiming at a porosity in the 20% range it was essential to develop a new screen printing paste. The conventional paste uses cellulose as a binder. But this material is hygroscopic and therefore the water content is hard to control. The result is a not reproducible solid loading of the paste, implying a large scatter in porosity of the sintered cermet as mentioned above. With such a paste it is not possible to adjust low values of porosity as the samples tend to become gastight if the porosity falls below 20%. As a new binder, polyvinyl-butylal (PVB) was selected. It shows similar rheological properties as cellulose but is less hydrophilic. Thus anodes with a well defined thickness (adjusted in the range of 40 to 60 $\mu$m), defined porosity and low surface roughness could be screen printed and sintered (3, 4).

An essential increase of the solid loading of the paste could now be achieved by replacing the so far used monomodal YSZ powder ($d_{50}$-values 90 $\mu$m) with a bimodal powder ($d_{50}$-values 90 $\mu$m and 0.5 $\mu$m). The porosity could thus be reduced from 50% to 20%.

To further decrease the heterogeneously catalytic free Ni surface, powders of NiCr alloys instead of pure Ni were applied. The chromium content was selected in the range of 1 mol% to 10 mol%. Due to the presence of water vapour and carbon oxides in the fuel cycle of the SOFC generator, Cr tends to migrate to the surface of the metal particles to form oxide scales which inhibit the reforming reaction compared to a clean Ni surface.

### Performance Data of the New Anode Cerments

The performance of the new types of anode with respect to the electrochemical oxidation of hydrogen was characterized by measuring I-V-curves and impedance spectra of complete cells under load while a mixture of 50% hydrogen and 50% water vapour was applied as fuel. The cathode was supplied with pure oxygen to keep the overall impedance of the cell as simple and as small as possible. According to the DC impedance amplitudes measured at 950°C and presented in fig. 1, the two cerments with high solid loading show the same anode polarization resistance, the value of which is only 17% of that of the conventional cermet. Thus the electrochemical performance of the new...
cermets turns out to be far better than specified by target value (0.10 Ωcm²).

These results are further confirmed by the I-V-curves measured with complete cells under the same fuel composition and temperature (fig. 2). The cathodes were supplied with pure oxygen to emphasize the anode's contribution to the overall cell resistance.

The major achievement realized with the newly developed anodes is demonstrated by fig. 3: the Arrhenius plots of the reforming rate constants show that the "cloud" characterizing the conventional cermet runs far away from the target region (corresponding to a methane turn-over equivalent to 0.5 A/cm² and a temperature range between 850 and 950°C). At 950°C the rate is 100 to 1000 times faster than required, and it would need temperatures far below 700°C to slow it down as desired. But obviously the increase of the solid loading is sufficient to shift the plot almost to the edge of the target region. It seems as if the interior Ni-surface of the cermet layer is hardly accessible to the gas because a plane sheet of Ni yields nearly the same data.

A considerable further decrease of the reforming rate is achieved by replacing Ni with NiCr alloy. Now the extrapolation of the experimental data hits the center of the target region (measured values directly within the target region do not exist because the turn-over tended to be unstable during experiments with very low flow rate of methane). The comparison with a smooth chromium oxide covered metal surface shows that a further reduction of the catalytic activity is still possible if required.

CONCLUSIONS

It was shown that the undesirably high catalytic activity of Ni-YSZ cermets for steam reforming of methane on the anode of SOFCs can be decreased by orders of magnitude. This is achieved by a decreased porosity of the cermet structure together with a replacement of the pure Ni with NiCr alloys. By this the kinetics of electrochemical hydrogen oxidation is even enhanced. Such anodes should be suited for on-anode reforming to avoid expensive stack integrated reformer units.
Current density in mA/cm²

Figure 2. I-V-curves of SOFC cells with different types of anodes: 950°C, fuel: 50% hydrogen, 50% water vapour/oxidant: pure oxygen.

Figure 3. Arrhenius plot of rate constant of methane reforming on various catalysts.

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REFERENCES

1. R. Leinfelder, Reaktionskinetische Untersuchung zur Methan-Dampf – Reformierung und Shift-Reaktion an Anoden oxidkeramischer Brennstoffzellen, p. 47, Universität Erlangen, Nürnberg, (2004).
2. I. Drescher, Kinetik der Methan - Dampf - Reformierung, p. 32, (1999).
3. T. Mezger, K. Wollny, Welt der Farben, 3, 11-15 (1996).
4. J. Will, Porous Support Structures and Sintered Thin Film Electrolytes for Solid Oxide Fuel Cells, Zurich, (1998).