INVESTIGATIONS INTO THE DEGRADATION OF THE CERMET ANODE OF A SOLID OXIDE FUEL CELL

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Today's SOFC membrane electrolyte assemblies produced within the Siemens SOFC development program and tested in mixtures of water vapor with hydrogen or methane show a long-term degradation of 20µV/h. This is still 10 times the rate required for a commercial application. As optical and electron micrographs of aged cells reveal, the nickel within the porous cermet structure of the anode disappears partially and accumulates in cracks of the cermet or on surfaces in the surrounding. It is concluded that nickel is transported via gaseous species. Thermodynamic calculations suggest that this is due to the volatile hydroxide Ni(OH)₂ and that the effect is enhanced by a high oxygen activity in the fuel.

INTRODUCTION

State of the art Siemens SOFC membranes were operated up to 2000 h at 950°C in mixtures of hydrogen and water vapor (1:1) or methane and water vapor (1:2). A long-term degradation of 20 µV/h was observed. The impedance spectra of aged cells showed an increase of the ohmic resistance and of the anode polarization. Fresh and aged anodes were compared by the appearance of their surfaces and by optical and scanning electron micrographs. Electrolyte membranes coated on both sides with anode cermet were placed in a gas stream of methane and water vapor (1:2, flow rate 2 to 5 m/s) to measure the rate of methane conversion over up to 600 h. The rate was found to be constant but the post test inspection of the samples revealed structural changes within the cermet.

RESULTS AND DISCUSSION

A screen printed layer of cermet is used as anode for the Siemens SOFC membrane. The cermet is a porous sintered structure consisting of equal volume parts of metallic nickel, 8 mole% yttria stabilized zirconia, and pores. The surface of a fresh cermet anode looks homogeneously gray. That of a cell which was operated at 950°C over 1000 h under a mixture of hydrogen and water vapor (1:1) looks hardly different despite its polarization resistance has doubled. Only very seldom a diffuse whitening of parts of the anode surface could be observed. The micrographs (optical and SEM) never revealed any structural change. This may be due to the fact that the electrical contact between two conducting bodies (be it the metallic contact between two nickel particles in the cermet or the electrochemically active contact between a nickel and an YSZ particle) breaks already when these bodies are separated by a distance in the range of an atomic diameter (10⁻¹⁰ m). A loss of matter within these dimensions can not be identified with polished
cross-sections under a microscope (optical or SEM). Only structural changes in dimensions of 1 μm will be detectable by these methods.

Changes visible already to the naked eye were observed when mixtures of methane and water vapor were applied. In this case the anode nearly always showed a white stripe, 0.5 to 2 mm wide, along the edge next to the fuel inlet as it is shown in fig. 1a. With increased magnification (fig. 1b) the bright spots in the dark looking cracks of the cermet layer were identified as shining crystals, up to 10 μm in diameter (fig. 1c). According to EDX analysis these crystals consisted of nickel. The remaining anode surface showed a weak increase of the gray scale in the direction from the fuel inlet to the fuel outlet. It was impossible to catch this change of color by a photography.

In fig. 2 two regions of a polished cross-section of this anode are compared. The first one (fig. 2a) shows a part of the white looking rim in fig. 1a, the second one (fig. 2b) shows a part inside the gray area to the left of the white rim. It is obvious that the number of (bright shining) nickel particles is considerably reduced within the white rim and it seems that the loss of nickel there is more pronounced near the fuel exposed surface of the cermet layer. This loss of nickel can explain an increase in ohmic resistance as well as an increase in anode polarization because electronic and electrochemical contacts are lost.

The findings concerning the nickel loss of the cermet are independent of the flow of electrical current. They do not only apply to loaded cells but also to stripes of electrolyte which were covered on both sides with the anode cermet and which were exposed over some 100 h to the flow of a mixture of methane and water vapor (1:2) at 950°C. The original purpose of this experiment was to measure the time dependence of the reforming reaction rate of the cermet. After the tests, the narrow glass pipes in which the catalyst samples were mounted, showed a dark deposit of nickel (identified by EDX and AAS) in the regions where the gas cooled down as it crossed the wall of the furnace. The deposit (some 10 μg) was larger the lower the conversion rate of the catalyst was.

These results unambiguously show that a transport of nickel via volatile species occurs. Therefore the partial pressures of gaseous nickel species were calculated. In the literature /1/ thermodynamic data of the following volatile nickel compounds in the system (Ni, C, O, H) were found: Ni(g), NiO(g), NiH(g), NiOH(g), Ni(OH)₂(g) and Ni(CO)₄(g). At 950°C and ambient pressure (1 bar) the mole fraction of carbonyl in pure carbon monoxide over metallic nickel is only 10⁻¹⁴. This compound is no longer considered because the other volatile species yield considerably higher partial pressures. As these compounds are free of carbon, the further discussion is based on the assumption that metallic nickel is in equilibrium with a gas mixture of hydrogen and water vapor at 950°C and at an ambient pressure of 1 bar. This gas can be characterized by its electrochemical potential versus oxygen of 1 bar.
The calculated mole fractions of volatile nickel species as a function of the oxygen potential are given in fig. 3. The oxygen activity is also shown and the corresponding mole fraction of water vapor in the mixture is indicated as well. In technical fuels, taking a fuel utilization of 80% into account, the SOFC anode has to operate in the oxygen potential range between -0.8 to -1.0 V. Above -0.68 V the anode would fail due to the loss of metallic conductivity caused by the oxidation of nickel. The hydroxide Ni(OH)$_2$ is the dominating volatile compound and its mole fraction increases along with the oxygen potential from $1 \times 10^{-10}$ at -1.0 V to $2 \times 10^{-8}$ at -0.8 V. The concentrations of volatile species increase with temperature as shown in fig. 4, where a constant gas composition of 34% hydrogen and 66% water vapor corresponding to an oxygen potential of 0.9 V at 950°C was assumed. The mole fraction of the hydroxide Ni(OH)$_2$ increases from $5 \times 10^{-12}$ at 700°C to $2 \times 10^{-9}$ at 950°C.

To get a feeling for the significance of these numbers, the rate of nickel loss caused by a flow of this gas at 950°C is calculated, assuming that thermodynamic equilibrium is achieved. Taking 500 sccm/min as a typical flow rate in the described experiments, a rate of nickel loss of $4 \times 10^{-11}$ g/s is found. After 1000 h this yields an amount of 0.16 mg nickel or a fraction of 0.11% of the mass of nickel in an anode 30 μm thick and 4x4 cm$^2$ in area. This value can not be considered as small if contacts are affected as was already stated above.

Concerning the microscopic inspection of cross-sections of anodes aged for 1000 h in the above mentioned gas, one can state the following. If the nickel loss is by kinetic reasons restricted to a certain volume of the anode which is predominantly attacked by the gas, then the size of this volume related to the volume of the anode would be also 0.11% after 1000 h. This corresponds in the case, that only a stripe along the edge of the anode is affected, to a width of this stripe of 45 μm and in the case that a layer of the anode is affected, to a thickness of this layer of 0.03 μm. If the equilibrium in the gas is not established the changes become even smaller. A structural change of the anode becomes visible by the microscope when the thickness of the affected volume becomes comparable to the size of the nickel particles (1 μm). Therefore it is obvious that after 1000 h under the above mentioned typical test conditions a nickel loss of the cermet can be detected at most by the microscope if it is located along the edge of the anode. This result fits to the fact that in long-term experiments with hydrogen water vapor mixtures hardly any change of the cermet structure could be observed.

On the other hand, the influence of the oxygen potential on the volatility of nickel (fig. 3) elucidates the observed high loss of nickel in the anode at the fuel entrance when a mixture of methane and water vapor is applied. Due to the absence of a catalyst (the cell housing and the gas pipes are made from pure alumina), the gas enters the cell still unreformed, what was proved by gas analysis. Therefore the oxygen potential which is proportional to the negative logarithm of the hydrogen concentration attains its maximum value at the fuel entrance of the cell and decreases most rapidly during the formation of the first percent of hydrogen by the reforming reaction. Correspondingly
high is, due to fig. 3, the tendency to form Ni(OH)₂. The onset of hydrogen production quickly reduces the equilibrium concentration of the hydroxide, so that nickel has to condense already close to the site where it became volatile. The metal should precipitate wherever the gas hits a surface and especially where the flow is low. This may explain the formation of large nickel particles in the cracks of the cermet. In any case at high flow rates a large part of the gas passes the catalyst unconverted so that the oxygen potential remains high (compared to a mixture of H₂:H₂O = 1:1 where even microscopic evidence for a nickel loss was quite rare) and correspondingly large is the amount of nickel that can precipitate according to fig. 4 when the gas is cooled down outside the furnace.

In the technical application for reasons of system and process engineering the cells will be fed with pre-reformed methane. Therefore the oxygen potential in such a gas will be already low compared to unreformed methane and the tendency for nickel volatilization will be decreased.

CONCLUSIONS

Strong evidence is given that the aging of SOFC anodes observed at Siemens is due to the loss of nickel via a volatile hydroxide. According to thermodynamic calculations it should be possible to reduce the effect by lowering the operating temperature and by avoiding oxygen potentials at the anode higher than the value (-0.8 V) given by the fuel utilization (80%). With respect to methane as fuel this implies that the gas should be partially reformed.

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REFERENCES

1. O. Knacke, O. Kubaschewski, K. Hesselmann, Thermochemical Properties of Inorganic Substances, Springer Verlag Berlin, Verlag Stahleisen m.b.H. Düsseldorf, 2. edition, 1991.
Ni: 50.8 wt.\%  
Zr: 38.0 wt.\%

Fig. 1a: Anode cermet near fuel gas inlet: change after 2000 h of operation under methane and water vapor, optical microscope.

Ni: 28.8 wt.\%  
Zr: 51.0 wt.\%

Fig. 1b: Enlargement of fig. 1a: formation of nickel crystals in the cracks of the anode layer, optical microscope.

Fig. 1c: Enlargement of fig. 1b: nickel crystals in a crack of the anode layer, SEM.
Fig. 2a: Cross-section of the anode layer within the white rim shown in fig. 1a.

Fig. 2b: Cross-section of the anode layer within the gray colored area shown in fig. 1a.
Fig. 3: Mole fractions of volatile nickel species in chemical equilibrium with a hydrogen / water vapor mixture over metallic nickel (T=950°C, p=1.0 bar): dependence on electrochemical potential of oxygen with reference to pure oxygen of 1 bar.

Fig. 4: Mole fractions of volatile nickel species in chemical equilibrium with a hydrogen / water vapor mixture over metallic nickel: dependence on temperature (p=1.0 bar, 34% H₂ / 66% H₂O).