PRODUCTION AND CHARACTERIZATION OF VACUUM PLASMA SPRAYED ANODES FOR SOLID OXIDE FUEL CELLS

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ABSTRACT

Cermet anodes produced by vacuum plasma spraying were developed for a new SOFC design. Various YSZ-Ni anodes using different starting materials and plasma spraying conditions were deposited onto 1 mm and 0.64 mm thick YSZ/(La,Sr)MnO3 half cells. The electrochemical characterization of these cells in the temperature range 800-950 °C includes U-i- and IR-drop measurements and impedance spectroscopy at different operation conditions. The results are correlated with the fabrication parameters and compared to screen printed anodes. The overall losses in the cell are divided and attributed to the different cell components.

INTRODUCTION

Recent investigations have shown that the performance of solid oxide fuel cells (SOFC) can be improved by using very thin electrolytes (1,2). Low internal resistances in the cells enable the reduction of the operating temperature, thus reducing the thermal load on the materials used. As a consequence, cheaper materials can be applied and the long-term stability of the cells can be improved (3).

Up to now different techniques have been applied to produce the SOFC components. Most of them are either very time-consuming or expensive. The vacuum plasma spraying process is a very useful materials processing tool to produce thin layers with controlled and graded porosity and composition. Vacuum plasma spraying has a high potential for the production of a new SOFC design with a very thin electrolyte (4,5). The details of the development of the plasma sprayed SOFC components at the DLR Stuttgart are described in the present proceedings (6).

A specific problem of the entirely plasma sprayed membrane-electrode-assembly (MEA) is the fabrication of the porous ZrO2-Ni fuel electrode. An open porosity of about 30 Vol.% is needed for a good gas permeability for both the fuel gas supply to and the removal of the gaseous reaction products from the electrode/electrolyte interface.
A composition of approximately 70 wt.% ZrO$_2$ / 30 wt.% Ni is necessary to fit the thermal expansion mismatch between the anode and the electrolyte, to stabilize the porous structure at the high operation temperatures and to provide sufficient electrical conductivity in the anode.

The evaluation of the performance of the plasma sprayed electrodes requires an overall electrochemical characterization under operating conditions. A very important aspect is the investigation of the correlation between the fabrication process conditions and the electrochemical behaviour of the anodes. Additionally, this paper compares the sprayed anodes with high performance screen-printed anodes. The influence of the operating conditions on the behaviour of the cells is outlined.

**EXPERIMENTAL**

**Vacuum Plasma Spraying of the SOFC Anodes**

The plasma spraying process is based on the generation of a plasma flame consisting of Ar or Ar with admixtures of H$_2$, N$_2$ or He, which are ionized by a high current discharge in the plasma torch. Powder which is injected into the plasma is accelerated and melted in the fast plasma jet. Carrying out the spraying process in low pressure atmosphere (50 - 250 mbar) results in longer laminar plasma jets with higher velocities and reduced interaction with the surrounding cold gas. The coating is formed by solidification and flattening of the fast particles at impact on the substrate. The velocity and degree of melting of the particles can be adjusted by the spraying conditions. This enables the fabrication of either very dense or controlled porous layers.

Four different approaches were carried out to get anode layers with the desired properties: Firstly, an agglomerated YSZ-30 wt.% Ni powder (10-40μm, Medicoat AG, Switzerland) was used. Secondly the YSZ (10-25μm, Medicoat AG) and the Ni powder (10-40μm, Sulzer-Metco, Switzerland) were injected separately into the plasma jet. Both methods are based on the control of the electrode's microstructure by the spraying conditions (e.g. torch nozzle, plasma gas, torch power, chamber pressure, spray distance etc.). Thirdly, NiAl 50/50 wt% (10-50μm, H.C. Starck, Germany) and YSZ powders were deposited simultaneously on the substrate. The porosity in the layer was formed subsequently by leaching out the Al content with a KOH solution. With the fourth method YSZ and NiO powders (10-30μm, Cerac, USA) were sprayed together; the NiO was reduced afterwards with hydrogen to pure Ni.

In order to study the influence of the spraying conditions, the coatings were deposited on grit blasted Ti-substrates. For the electrochemical measurements, the anodes were sprayed onto sintered electrolyte plates (Figure 1) consisting of cubic stabilized zirconia (ZrO$_2$-8 Vol.% Y$_2$O$_3$, Kerafol GmbH, Germany). The electrolyte substrates with a
diameter of 35 mm had a thickness of 1 mm and 0.65 mm respectively. Screen printed layers of (La_{0.8}Sr_{0.15})MnO_3 (Siemens AG, Germany) were used as cathodes. These YSZ-(LaSr)MnO_3 half cells were preheated electrically up to 600 °C prior to the deposition process in order to avoid cracking due to thermal stresses.

Characterization of the Plasma Sprayed Anodes

Microstructure and Phases. The metallographically prepared anode samples were examined by light microscopy and scanning electron microscopy (SEM). The elements were detected by energy dispersive X-ray microanalysis (EDX). The phase contents and the porosity were determined by quantitative image analysis. Additionally the porosity and the pore size distribution were evaluated by gas adsorption and mercury porosimetry. The different phases in the anodes were investigated by X-ray diffraction. The cells were examined with these methods before and after electrochemical characterization in order to analyze the degradation of the microstructure.

Electrochemical Characterization. The test equipment for the electrochemical characterization of the cells is shown in Fig. 2. The components are:

- a furnace (T_max = 1200 °C) with an internal ceramic housing for the cell
- a control unit for the process gases, the temperature and the pressure
- a computer controlled data acquisition system with electronic load
- an frequency response analyzer
- an oscilloscope with a fast on/off switch for the IR drop measurements

In the furnace the cell is located in a ceramic housing whose parts are shown in Fig. 1. Hydrogen and oxygen are fed to the anode and cathode, respectively. Gas distribution plates ensure uniform gas flow over the entire electrode areas. The cell is sealed with gold rings and sealing weights. Platinum nets were used to contact the electrodes electrically. The electrochemical characterization of the cells included:

- U-i-measurements
- impedance spectroscopy
- current interruption measurements
- investigation of the cell stability at constant current load up to 200 h
- 4-point electrical conductivity measurements in the temperature range 20-1000 °C

The cell was operated at temperatures between 800 °C - 950 °C. The fuel gases used were H_2, H_2 + H_2O, H_2 + N_2 with a flow rate of 0.5 SLPM (standard liter per minute). Oxygen and air with a flow rate of 0.5 SLPM were used as oxidant gases.
RESULTS AND DISCUSSION

Microstructure of the Anodes

The anodes which were sprayed with the ZrO₂ - 30 wt.% Ni (Figure 3) and the ZrO₂ + Ni powders revealed mean porosities of about 15 Vol.% and ZrO₂ / Ni contents of approximately 65/35 Vol.% (image analysis). It was observed that the pores between the ZrO₂ particles were closed by the molten Ni particles. This problem could be solved for the ZrO₂ + Ni anodes by adjusting the degree of melting of the Ni particles by selection of a proper position of the powder feed injection port. Due to the lamellar microstructure, the in-plane electrical conductivity of the anodes was three orders of magnitude higher than the literature data (7).

The ZrO₂ + NiAl anodes (Figure 4) show a very fine, interconnected porosity after leaching out the Al. With gas adsorption porosimetry a specific surface area of 12 m²/g was determined. XRD measurements showed that the Ni₂Al₃ and the NiAl₃ phases of the NiAl alloy were completely transformed to pure Ni. The NiO + ZrO₂ anodes revealed a strong increase in porosity after the reduction of NiO to Ni. The porosity reached 28 Vol.% with an mean pore size of 200 nm (Hg-porosimetry). The NiO was completely reduced to Ni (XRD). Compared to the first two methods, it is easier using NiAl and NiO powders to produce anodes with open porosity.

The cross section of a entirely vacuum plasma sprayed MEA element on a Ni-felt is shown in Figure 5. The VPS-multilayer consists of an porous YSZ + Ni anode, a dense YSZ-electrolyte and a porous (La,Sr)MnO₃ cathode. In the next stage of development the thickness of the layers of the entirely plasma sprayed cells will be optimized.

Electrochemical Behaviour

Anode materials. A comparison of the cell performance of the plasma sprayed anodes and a screen printed anode (Siemens AG, Germany) at 950 °C is depicted in Figure 6. The electrolyte thickness of the cells was 1 mm. The ZrO₂ - 30 wt.% Ni and the ZrO₂ + Ni anodes show the same good performance as the screen printed one. Due to the thick electrolyte, the power density at 700 mV only reached 200 mW/cm². A maximum power density of 250 mW/cm² was obtained at a voltage of 600 mV.

Both, the ZrO₂ + NiAl and the ZrO₂ + NiO anodes have lower power densities. Metallographical examination showed that the electrodes were far too thick. Additionally the electrical conductivity was too low due to poor interconnection between the Ni crystallites and high porosity in the layers. More work has to be carried out including adjusting the electrode’s thickness and the phase distribution in the anodes.
Current Density of the Cell. Impedance spectroscopy was applied in order to examine the different cell components electrochemically. Fig. 7 shows a Bode-diagram of a cell with plasma sprayed ZrO₂ + Ni anode and an electrolyte with a thickness of 640 μm at 950 °C as a function of current density. The ohmic resistance in the high frequency range is approximately 100 mΩ. This corresponds to a specific conductivity of YSZ of 12 S/m in accordance with literature data (7). The total impedance in the low frequency range at i = 0 (open circuit voltage, OCV) amounts to 400 mΩ. The total impedance decreases with increasing current density to 240 mΩ at i = 230 mA/cm². The reason for that is the reduced polarization resistance of the electrodes following the Butler-Vollmer relation. The curve of the phase shift reveals an extended local maxima in the high and the low frequency range. These two phase shifts cover another smaller one in the middle frequency range. Consequently three time-dependent elements (e.g. RC terms) are necessary to describe the frequency response of the cell. The corresponding equivalent circuit is shown in Figure 8.

Process Gases. To separate the overall cell impedance into the single impedance components, a gas variation was carried out (Figure 9). Replacing the oxygen by air results in an increase of the impedance and of the phase shift in the low frequency range. The addition of N₂ to the fuel gas H₂ had nearly no influence onto the phase shift, whereas the humidification of the hydrogen leads to a strong decrease of both the impedance and the phase shift at the low and middle frequency range. The same observation was also reported by Jiang (8).

From these dependencies we can conclude that the RC term in the high frequency range corresponds to the charge transfer at the anode Rct(A). The charge transfer at the cathode Rct(C) occurs in the middle frequency range and in the low frequency range a kind of Nernst-term RN appears. RN is caused from the binary diffusion of H₂ and H₂O (9). Due to the overlapping of RN(A) and Rct(C) it is difficult to separate them properly.

Electrode Potentials. The fit of the equivalent circuit to the measured impedance spectrum enables the determination of the values of the single impedances. The electrode potentials and the cell voltage can be calculated from the product of these impedances and the current densities (Fig. 10). At 220 mA/cm² the ohmic losses in the 640 μm thick electrolyte (100 mV) are about twice as high compared to the losses due to Nernst diffusion. Therefore we can expect a far higher performance of the entirely plasma sprayed cells with very thin electrolytes. The improved plasma sprayed anode reveals a very low anodic polarization of approximately 24 mV at 220 mA/cm² which is half the overvoltage of the cathode. The calculated cell voltage is in good agreement with the measured one.

Temperature. The temperature dependency of the performance of a cell with sprayed anode and a 640 μm thick electrolyte in the range 800°C - 950°C is shown in Figure 11. The power density decreases from 340 mW/cm² at 950°C to 60 mW/cm² at 800°C. Impedance spectroscopy at OCV showed a strong increase of the cathodic charge
transfer resistance and the ohmic resistance of the electrolyte. The corresponding conductivities in the Arrhenius-plot follow an exponential temperature dependency. The activation energies calculated from the slope of the curves are $E_A(C) = 160$ kJ/mol, $E_A(A) = 140$ kJ/mol and $E_A(YSZ) = 60$ kJ/mol. These results are in good agreement with literature data (7).

**Cell Stability at Constant Current Load (0-200h).** The cell voltage at 950°C and H₂/O₂ operation at a constant current density of 100 mA/cm² during the first 200 h is plotted in Figure 12. No measurable degradation of the plasma sprayed anodes was observed. After humidification of the fuel gas a decrease of the cell voltage of about 50 mV due to the lower hydrogen partial pressure was observed.

**CONCLUSIONS**

SOFC anodes were fabricated with the vacuum plasma spraying technique. Using different starting materials and adapting of the spraying conditions the required microstructure and porosity were adjusted successfully. The anodes which were sprayed with the separately fed ZrO₂ and Ni powders onto 1 mm thick electrolytes show the same good U-i behaviour as the screen printed reference anodes. The losses at the different cell components could be determined by impedance spectroscopy. The polarization losses of the improved plasma sprayed anodes operated at a current density of 200 mA/cm² are very low compared to those of the cathode and the 500 μm thick electrolyte. An electrochemical degradation of the sprayed anodes within the first 200 h of cell operation could not be observed. Future work will concentrate on the optimization of the microstructure and the thickness of the other MEA components (cathode, electrolyte) and the electrochemical characterization of the entirely plasma sprayed cells.

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Figure 1: SOFC cell (4) with a plasma sprayed anode and components for the electrochemical characterization (gas distribution plates (1,3), gold rings (2), Pt-nets (5), sealing weight (6)).

Figure 2: SOFC test equipment (furnace (1), operation control unit (2), computer controlled data acquisition system (3), impedance spectroscope (4), oscilloscope (5)).
Figure 3: Microstructure of a vacuum plasma sprayed ZrO$_2$ - 30 % Ni anode (white: Ni, grey: YSZ, black: pores)

Figure 4: Microstructure of a vacuum plasma sprayed ZrO$_2$ + NiAl anode after leaching out the Al (grey: YSZ, darker grey: Ni, black: pores)
Figure 5: Cross section of an entirely vacuum plasma sprayed MEA element (Ni-felt (bottom), ZrO$_2$-Ni anode, YSZ electrolyte, (La,Sr)MnO$_3$ cathode (top))

Figure 6: U-i behaviour of different plasma sprayed SOFC - anodes on sintered, 1mm thick YSZ-electrolytes and screen printed cathodes at 950°C
Figure 7: Bode-diagram of a SOFC cell with plasma sprayed ZrO$_2$ + Ni anode and 640 µm thick YSZ-electrolyte at 950°C as a function of current density.

Figure 8: Equivalent circuit of a SOFC cell.
Figure 9: Bode-diagram of a SOFC cell with plasma sprayed ZrO₂ + Ni anode and 640 μm thick YSZ-electrolyte at 950°C and OCV as a function of process gases.

Figure 10: Voltage losses at the components of a SOFC cell with a plasma sprayed ZrO₂ + Ni anode and a sintered, 640μm thick YSZ-electrolyte at 950°C.
Figure 11: U-i behaviour of a SOFC cell (YSZ: 640μm) with a plasma sprayed ZrO$_2$ + Ni anode as a function of temperature.

Figure 12: Time dependence of the voltage of a SOFC cell (plasma sprayed ZrO$_2$-30%Ni anode, 640 μm thick YSZ-electrolyte) at a constant current density of 100 mA/cm$^2$.

Electrochemical Proceedings Volume 97-18