IMPROVED MATERIAL COMBINATIONS FOR STACKING OF SOLID OXIDE FUEL CELLS

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ABSTRACT

During the operation of a solid oxide fuel cell stack with metallic interconnect plates, oxide scales are formed at the surface of the interconnect material leading to an electrical insulating effect.

In the present work, the electrical contact resistance between different ferritic interconnect steels and contact materials was studied at 800°C as a function of aging time. The contact materials consisting of a perovskite-type oxide and Ni mesh were tested under cathodic (air) and anodic (Ar/4 vol.% H₂/3 vol.% H₂O) conditions. The results reveal that ferritic steels doped with reactive elements of La and Ti exhibit oxide scales with the highest electrical conductivity and the lowest increase of contact resistance with time. Elements as Al and Si lead to an increase of the contact resistance. After the contact resistance measurements, polished cross sections of the samples were investigated by scanning electron microscopy.

INTRODUCTION

In order to achieve high voltages for stationary energy generation, the individual solid oxide fuel cells (SOFCs) must be electrically connected in series to form a stack. Metallic interconnect plates for this application have to meet the following demands: (a) excellent chemical compatibility and stability, (b) high oxidation resistance, (c) appropriate thermal expansion coefficient and (d) high electrical conductivity. Under operating conditions, electrically insulating oxide scales such as Cr₂O₃ or Al₂O₃ are generated at the interconnect surface. In order to minimize the electrical losses, the formation of the oxide scales on the interconnect surface must be prevented or the oxide scales formed must have sufficient electrical conductivity. Apart from high electrical conductivity, the oxide scales formed should show a limited chemical interaction with the adjacent contact materials and should not release volatile chromium species which lead to a rapid degradation of SOFC performance.

Alloys based on Fe-Cr are suitable materials for interconnect plates [1,2]. Ceramic pastes or metal meshes are usually applied between the electrodes and interconnect plates for electrical contact, and at the same time, to compensate tolerances of manufacturing of the components. For this purpose, the cell stack is subjected to a heat treatment in a joining process, during which the pastes are sintered and the metal meshes are bonded onto the adjacent components due to diffusion processes.

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Under the operating conditions of the SOFC, the contact layers must exhibit high electrical conductivity, a thermal expansion matching those of the other cell components, as well as chemical stability and chemical compatibility with the adjacent components [3,4]. Suitable contact layers are lanthanum manganites (LaMnO3) or lanthanum cobaltites (LaCoO3) [5,6]. In the cathode compartment, the steel underneath the cathode contact layers corroded by flowing air. The slowly growing oxide scales, composed of Cr2O3, Fe2O3, Al2O3 or SiO2, usually have a low electrical conductivity and cause a loss of power output of the cell stack. Rapid growth leads to their detachment and a sudden high loss of power output.

Moreover, chemical reactions which are difficult to control, take place between the oxide scales formed on the steel and the contact layers. In this way, new chemical phases are formed and usually also have a low electrical conductivity.

In order to prevent a degradation of the SOFC stack from aging and to achieve a constantly high power density, the Ohmic resistances of the stack must not change during operation, i.e. the interconnect as well as possibly forming corrosion scales should always have a high electrical conductivity as the electrically conducting link between the individual cells. The investigations therefore aim at finding new interconnect/contact layer material combinations which fulfil these requirements.

For this purpose, the electrical resistances between interconnect plate and ceramic contact layer and between interconnect plate and Ni mesh was measured as a function of aging time under cathodic and anodic conditions, respectively. Subsequently, the chemical interactions and the stability of the specimens were determined by scanning electron microscopy.

**EXPERIMENTAL**

The model steels used are termed FeCr(Mn), FeCr(Mn,La,Ti), FeCr(Mn,Si) and FeCrAl(Si,Mn) according to their chemical composition. The FeCrAl(Si,Mn) steel (material number 1.4742 / X 10 CrAl 18) is currently used as interconnect material [7].

Specimens of 10 mm x 10 mm x 2 mm and 15 mm x 15 mm x 6 mm were cut from steel plates for experiments under cathodic and anodic conditions, respectively. These specimens were then finely ground on all sides using 1200 grid abrasive paper. For some experiments the steel was preoxidized by exposing the steel specimens for 100 h to a temperature of 800°C in air (partial pressure of oxygen p(O2) = 0.21 atm) or in reducing atmosphere with p(O2) = 10^-15 atm. The material for the ceramic contact layers was a cobaltite-based perovskite powder. The powder was processed into viscous paste by means of binders and solvents, screen-printed onto the steels and dried at 60°C. The layers were about 100 μm thick and are termed in the following as CCC2 (ceramic cathodic contact, batch 2).

For measuring the electrical resistance under cathodic conditions, two coated metal plates were sandwiched to obtain the following configuration: metal/contact layer/contact layer/metal. Under anodic conditions, the following sandwich configuration was selected for the experiments: metal/Ni mesh/anode(Ni/YSZ)/Ni mesh/metal (Fig. 1). Two
platinum wires were spot-welded onto each of the metal platelets and then connected to the current source and the potentiostat.

![Diagram of experimental sandwich arrangement](image)

**Fig. 1** Experimental sandwich arrangement for contact resistance measurements under cathodic and anodic test conditions.

The electrical resistance of the specimens was measured using a four-probe dc technique. For this purpose, a constant current density of 150 mA/cm² flew through Pt wires 3 and 4 (Fig. 1), while the voltage drop at the sample arrangement was measured by Pt wires 1 and 2. The contact resistance, i.e. the resistance per unit area, results from Ohm’s law and the specimen’s in-plane cross-sectional area. The voltage drop at the specimens was measured as a function of time at 800°C in a constant atmosphere. The cathodic test conditions corresponded to air (static), so that p(O₂) = 0.21 atm. In order to simulate the anodic operating conditions, a mixture of Ar/4 vol% H₂/3 vol% H₂O was passed through the tube furnace, and an oxygen partial pressure of p(O₂) = 10⁻¹⁵ atm was established through the H₂ + ½O₂ ⇌ H₂O water-hydrogen equilibrium. After the specimens were installed in the furnace, they were heated at 100 °C/h up to 800°C. Subsequently, a constant current density of 150 mA/cm² was passed through the specimens and the voltage drop at the specimens was recorded every hour.

After termination of the exposure, the specimens were embedded in resin, cut in the transverse direction of the sandwich layers, polished and post-examined using a scanning electron microscope.

**RESULTS AND DISCUSSION**

**Ceramic Cathodic Contact**

Fig. 2 shows the electrical resistances of the preoxidized model steel/CCC2 material combinations. It can be seen that those material combinations with Fe-Cr model steels containing La and Ti doping (FeCr(Mn,La,Ti) exhibit the lowest electrical resistances. Material combinations with Fe-Cr model steels without La and Ti (FeCr(Mn), show slightly higher resistances, whereas the commercial FeCr(Mn,Si) and FeCrAl(Si,Mn) steels display a very high electrical resistance.

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Fig. 2 Electrical resistances of material combinations composed of CCC2 together with FeCr(Mn,Si), FeCr(Mn), FeCr(Mn,La,Ti) and FeCrAl(Si,Mn) (experimental conditions: T = 800°C, p(O2) = 0.21 atm, i = 150 mA/cm². Preoxidation of the steels: T = 800°C, p(O2) = 0.21 atm, t = 100 h).

The following sequence of oxide scales could be identified for all model steels after exposure in air: CCC2/MnCr2O4/CaCrO4/Cr2O3/model steel. The FeCr(Mn,La,Ti) steel, moreover, showed considerable internal oxidation forming TiO2 and La2O3. However, the FeCrAl(Si,Mn) steel formed an additional insulating alumina layer between the steel and the reaction zone with the ceramic contact material and the FeCr(Mn,Si) steel an SiO2 layer in the immediate vicinity of to the metal due to its high Si content. Al2O3 and SiO2 have very poor conductivity, which is probably the reason for the relatively high electrical resistances (Fig. 2).

Fig. 3 Scanning electron micrograph of the FeCr(Mn)/CCC2 material combination after resistance measurement (T = 800°C, p(O2) = 0.21 atm, i = 150 mA/cm², t = 500 h).
Detecting the concentration distribution of Cr, Mn and Ca from energy-dispersive X-ray analysis, it is easily possible to derive the position of the MnCr2O4, CaCrO4 and Cr2O3 oxide phases as shown in Figs. 3 and 4. It can also be seen in Fig. 4 that Ti concentrates at the metal/Cr2O3 phase boundary but is also dissolved in the Cr2O3 layer. If Ti4+ ions are incorporated into the crystal lattice of Cr2O3 [8], ionic and electronic defects are formed, which could account for the decreased electrical resistance of the FeCr(Mn,La,Ti)/CCC2 material combination.

Furthermore, Fig. 4 clearly shows the internal oxidation of the the FeCr(Mn,La,Ti) model steel involving the formation of TiO2 and La2O3. With respect to the Mn concentration distribution, it is striking to note that Mn accumulates as a MnCr2O4 layer directly adjacent to the contact layer. This is of elementary significance for the problem of chromium vaporization in the SOFC. Since the activity of the Cr2O3 in the MnCr2O4 spinel is reduced by about one order of magnitude, the spinel acts as a kind of protective layer and reduces chromium vaporization [1,9].
Fig. 5 shows the scanning electron micrograph of the FeCr(Mn,Si)/CCC2 material combination after resistance measurement. Here the high concentration of Si leads to a low electrical conducting SiO2 scale during operation (cf. Fig. 2).

In the further course of the experiments, non-preoxidized model steels were investigated. Fig. 6 shows the electrical resistances of the FeCr(Mn)/CCC2, FeCr(Mn,La,Ti)/CCC2 and FeCr(Mn,Si)/CCC2 material combinations as a function of aging time. It can be seen that in this case the material combination with FeCr(Mn,La,Ti) also provides the lowest resistances.

![Fig. 6 Electrical resistances of the polished non-preoxidized FeCr(Mn)/CCC2, FeCr(Mn,Si)/CCC2 and FeCr(Mn,La,Ti)/CCC2 material combinations (T = 800°C, p(O2) = 0.21 atm, i = 150 mA/cm², t = 500 h).](image)

The material combination with the FeCrAl(Si,Mn) steel is not shown in Fig 6 because the electrical contact resistance is about one order of magnitude higher and exceeds 1000 mΩ cm² after few hours at 800°C. This is related to the formation of a thin Al2O3 scale directly on the steel, which has a strong electrically insulating effect. The increased resistance of the material combination with FeCr(Mn) in comparison to FeCr(Mn,La,Ti) can be explained by the composition of the Cr2O3 scale as mentioned above. A correlation between layer thickness and resistance could not be found.

**Metallic Anodic Contact**

In the following the electrical resistance measurements are presented which were performed under anodic conditions, i.e. p(O2) = 10⁻¹⁵ atm established with a mixture of Ar/4 vol% H2/3 vol% H2O. Only the results of the most promising candidate of the model steels, FeCr(Mn,La,Ti) are presented here. Fig. 7 shows the electrical resistances material combinations with differently treated steel as a function of aging time. It can be seen that the preoxidation of the steel leads to significantly higher electrical resistances than for not preoxidized steel. As can be seen in Fig. 8, the non-preoxidized specimen forms welding points between Ni mesh and steel. For this reason, the electrical resistance
is low and hardly changes with time. It should be noted, however, that oxidation occurs at the outer interface between steel and Ni mesh to a limited extent. It must therefore be feared that the good electrical contact between Ni mesh and steel may vanish in the long term because an electrically insulating Cr₂O₃ scale is formed. After preoxidation in air, the Cr₂O₃ layer was already formed and resulted in poor electrical conductivity during measurement in anodic atmosphere. Also the sample preoxidized in anodic atmosphere showed high initial electrical resistivity but with a much faster approach of the values determined with the polished sample (Fig. 7).

![Fig. 7](image)

**Fig. 7** Electrical resistances of the FeCr(Mn,La,Ti) model steel differently treated and measured in Ar/4 vol.% H₂/ 3 vol.% H₂O. (T = 800°C, p(O₂) = 10⁻¹⁵ atm, i = 150 mA/cm²).

![Figs. 8](image)

**Figs. 8** Scanning electron micrographs of interfaces of polished non-preoxidized FeCr(Mn,La,Ti)/Ni (a) and preoxidized FeCr(Mn,La,Ti)/Ni (b) after contact resistance measurement under anodic conditions (T = 800°C, p(O₂) = 10⁻¹⁵ atm, i = 150 mA/cm², t = 250 h).

One reason for the preoxidation of the steels is to prevent interdiffusion between steel and Ni mesh. Whereas Fe diffuses from the model steel into the Ni mesh, Ni diffuses
from the Ni mesh into the model steel forming local austenitic areas with higher thermal expansion coefficients.

The electrical resistances of the preoxidized model steels are initially very high. When the steel is preoxidized under anodic conditions, the resistance strongly decreases with aging time but even after 250 hours it is still much higher than for specimens that have been polished and not preoxidized. The model steel preoxidized in air shows very high resistance from the very beginning and only drops very slowly as a function of time.

A possible explanation for these differences in behavior is given by the data in Fig. 9. Whereas Mn$_2$O$_3$ is formed on the steel in air, MnO is formed on the surface in H$_2$/H$_2$O atmosphere. Both manganese compounds have different electrical conductivity and different oxide growth rate resulting in different layer thickness.

![Fig. 9](image)

**Fig. 9** XRD patterns of the oxide scales on FeCr(Mn,La,Ti) steel, exposed at 800°C in air and in Ar/ 4 vol.% H$_2$/ 3 vol.% H$_2$O (p(O$_2$)=10$^{-13}$ atm.

**SUMMARY AND CONCLUSIONS**

Aluminium-containing steels tend to form Al$_2$O$_3$ scales on the surface under SOFC operating conditions, i.e. in oxygen partial pressures of 10$^0$-10$^{18}$ atm at 800°C. On the one hand, the Al$_2$O$_3$ scales offer the advantage of reducing the oxidation rate and the vaporization of chromium species. On the other hand, they increase the electrical contact resistance between the electrodes and interconnect plate. The present studies show that a good compromise between oxidation resistance and good electronic conductivity of the oxide can be achieved with steels of the type FeCrMn(La,Ti).

The electrical contact resistances depend on the type of contact layer, on the composition of the steel and on the pretreatment of the steel. Whereas a plateau is nearly
always reached in contact resistance measurements with the FeCr(Mn) and FeCr(Mn,La, Ti) steels, i.e. the electrical resistance only changes slightly with time, an almost linear increase of resistance with time was found for FeCrAl(Si,Mn) and FeCr(Mn,Si).

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