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Area specific resistance of oxide scales grown on ferritic alloys for solid oxide fuel cell interconnects

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ABSTRACT

Planar solid oxide fuel cells (SOFC) are considered to be power generators with high efficiency and low emission at small power units (1–200 kW_{el}). Many prototype systems are already successfully realized. For mass production the costs have to be reduced and the long-term stability has to be enhanced. Power losses <0.5%/1000 h is the target value for stacks in stationary SOFC-based power systems. To reach this goal, the factors influencing degradation have to be found and reduced. In this work the interaction between interconnect and different ceramic materials such as perovskites ($La_{0.8}Sr_{0.2}(Mn,Co)O_3$, $La_{0.65}Sr_{0.3}MnO_3$, $La_{0.65}Sr_{0.3}(Mn,Co)O_3$) and spinels ($Mn(Co,Fe)O_4$, $(Cu,Ni)Mn_2O_4$) was investigated on the cathode (air) side of conventional ferritic interconnect materials (CroFer22APU, ITMLC, ZMG232L). The method to determine the value of the area specific resistance between interconnect and contact layer ($R_{\#ICC}$) within a tolerance of 10% has been developed to provide reliable data for ASR values and their degradation.

The $R_{\#ICC}$-value increases with annealing time. The degree of this increase depends on used materials and their combination. The spinel contact layers form a thin dense ceramic layer at the beginning of the annealing process. This layer reduces the oxidation rate of the alloy. Because of this protection layer a thinner oxide scale grows and the ASR aging rate is much lower (0.4–0.9 $m\Omega\,cm^2$/1000 h). The comparison of the aging rates of different alloys with $La_{0.8}Sr_{0.2}(Mn,Co)O_3$ contact layer reveals remarkable differences: 3.1 $m\Omega\,cm^2$/1000 h for CroFer22APU, 10.9 $m\Omega\,cm^2$/1000 h for ITMLC and 21.2 $m\Omega\,cm^2$/1000 h for ZMG232L.

The degradation in a stack has been determined from the $R_{\#ICC}$-values and geometric factors. The impact of oxidation at the cathode side of interconnect is about one third of the total stack degradation. The method opens the possibility for comparing area specific resistances of special material combinations with high accuracy. By optimized material combinations the degradation in stacks can be reduced to <0.5%/1000 h.

1. Introduction

Planar, bipolar SOFC needs interconnects for separating gas and air flow, electrical contacting and mechanical stabilization of the cells in stack. In the past years several types of ferritic stainless steels have been examined as potential candidates for stack interconnects, because of their low resistivity of oxide scale, easy processing and low-cost manufacturing. The thermal expansion coefficient (TEC) of the ferritic alloy Crofer22APU [1,2] is well suited to the TEC of the electrolyte and the material has a sufficient stability at temperatures about 800 °C.

At high temperatures oxide layers grow on the surface of ferritic stainless steels. The oxide scale with relatively good electrical conductivity protects alloy from chromium evaporation and breakaway oxidation. Ceramic protection layers affect the oxide formation at the interconnect and are important for the long-term operation of a stack. The oxide layers grow under typical SOFC operating conditions with rising time, cause an increase of the area specific resistance (ASR) and are partially responsible for stack degradation. Many efforts were made to diminish disadvantages of using ferritic alloys for SOFC interconnect materials. The common strategy to minimize the oxide scale growth is the realization of a gas-tight, highly electrical conductive protection layer with a thermal expansion coefficient (TEC) matched to the interconnect. Different coatings were tested in order to ascertain the most suitable SOFC interconnect protection and contact material.

Perovskites (ABO_3) with lanthanum and strontium on the A-site and manganese on the B-site as well as different manganese, cobalt, or copper-based spinel materials offer relatively good

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Table 1
Selected ferritic alloys for investigations.

Name	Charge	Manufacturer	Date of delivery
Crofer22APU	170845	Thyssen Krupp VDM	06/2006
ITMLC	007	Plansee SE	08/2006
ZMG232L	LM647	Hitachi Metals LTd.	12/2006

chemical stability, high electrical conductivity and a TEC near to the interconnect and electrolyte one.

There are different approaches for measuring the ASR values of the oxide scale formed between ferritic alloy and ceramics. However, the measured ASR values are actually a sum of different resistances consisting of interconnect-, contact layer- and oxide scale resistances. The separation of those different parts of resistances is complicated. A great scattering of absolute ASR values and their change with the time appears due to various assemblies of samples and different material compositions [3]. For example, the ASR values of the oxide scale for similar material combinations ($La_{0.8}Sr_{0.2}(Mn,Co)O_3$ and CroFer22APU) range from 0.8 to 12 mΩ cm^2 [4–7]. The rate of the ASR value increment of the oxide scale is very important for the estimation of the degradation of a stack. This rate varies from 0.5 to 25 mΩ cm^2/1000 h for above mentioned material combination and shows the importance to find appropriate samples to measure reliable ASR values and their behavior over time.

The goal of this work is to calculate a contribution of ASR of oxide scale in contact with ceramic layer to the total ASR of the stack and to degradation rate for different interconnect materials. We demonstrate an approach for the determination of ASR of the oxide scale and show the impact of appropriate material combinations of different alloys with protection or contact layer on the degradation rate of ASR due to oxide scale growth.

2. Experiments

2.1. Oxidation investigations of Crofer22APU, ITMLC and ZMG232L

We investigated the formation of the oxide scale on the surface of metallic interconnect after oxidation in air atmosphere to find a correlation between resistance increase and parameters of the oxide scale. An important reference value for the metallic interconnect materials is the weight gain of the sample. The samples of the size 15 mm × 15 mm × 0.5 mm were prepared from different ferritic alloys (Table 1) and were annealed at 850 °C for different times to evaluate the oxidation behavior parallel to the ASR measurements. Nine specimens were prepared from each ferritic alloy for different oxidation duration. Three of nine samples were coated with LSMC perovskite protective layers by roll-coating. The uncoated and coated samples were annealed in air at 850 °C. The first set of specimens was removed from the furnace after 800 h and the next ones after 1600 h and 3200 h. The weight gain of each sample was determined by a Sartorius (LA 230 s) balance before and after annealing. For comparison the values were normalized to the surface area of the sample.

2.2. Measurements of ceramic contact layer

A four-point probe method was used to measure the resistivity of the low temperature sintered contact layer materials (Fig. 1). The measurements were performed under static air conditions comparable to the measurements in [8]. Minimum two samples for each combination were measured and the average values were calculated.

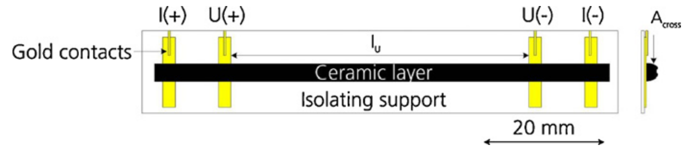

Fig. 1. Schematic diagram of the sample with ceramic rib made of paste to measure the resistivity of low temperature sintered ceramic.

The temperature in the furnace corresponds to the joining profile of the stack (920 °C/2 h → 850 °C/800 h). The measurements were carried out with thermal cycles after 800, 1600, and 3200 h of oxidation. A constant current of 0.1 A with offset compensation was applied. The resistivity ρ_{Meas} was calculated using the equation (1):

$$\rho_{Meas} = R_{Ohm} \cdot \frac{A_{cross}}{l_U} \qquad (1)$$

where R_{Ohm} is the measured resistance, A_{cross} is the cross section area of the sample, and l_U is the distance between the potential contacts.

A profilometer (Fries Research Technologies GmbH) was used to determine the cross section area. For this purpose, the height profile of the ceramic rib was recorded on five different points. The cross section area was defined by integration. The uncertainty for the resistivity measurement given by such estimation of cross section area was ±4.6%.

A four-point probe resistance measurement, where corresponding current and voltage wires were directly connected to the ceramic layer, insures that contacting of ceramic ribs influences neither the absolute value nor long-term behavior of the resistance. Three different perovskites: $La_{0.8}Sr_{0.2}Mn_{0.9}Co_{0.1}O_3$, $La_{0.65}Sr_{0.3}MnO_3$, $La_{0.65}Sr_{0.3}Mn_{0.9}Co_{0.1}O_3$ and two spinels: $MnCo_{1.9}Fe_{0.1}O_4$, $Cu_{0.6}Ni_{0.4}Mn_2O_4$ were chosen from a broad field of contact or protection ceramics [3,9–13]. They give information about influence of substoichiometry, different amount of strontium and presence of cobalt on ASR of the oxide scale. The compound $Cu_{0.6}Ni_{0.4}Mn_2O_4$ was synthesized from the binary oxides Mn_2O_3, CuO and NiO at temperatures 1050–1100 °C in air using a common solid state reaction process, the other powders for preparation of contact materials were supplied by company Staxera GmbH (Dresden, Germany).

In the following text the ceramic materials are abbreviated as:

$La_{0.8}Sr_{0.2}(Mn,Co)O_3$	LSMC
$La_{0.65}Sr_{0.3}MnO_3$	uLSM
$La_{0.65}Sr_{0.3}(Mn,Co)O_3$	uLSMC
$Mn(Co,Fe)O_4$	MCF
$(Cu,Ni)Mn_2O_4$	CNM

2.3. Measurements of ASR between interconnect and ceramic contact

The sample setup was optimized in several efforts and is illustrated in Fig. 2. The asymmetric assembly of current- and voltage contacts was chosen to keep the uniform current distribution

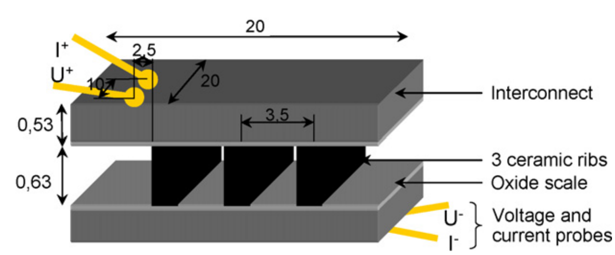

Fig. 2. Sample assembly for ASR measurements between interconnect and ceramic contact (dimensions in mm).