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Coated stainless steel 441 as interconnect material for solid oxide fuel cells: Evolution of electrical properties

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HIGHLIGHTS

- We exposed cerium/cobalt coated AISI 441 in a SOFC cathode side atmosphere.
- We tested two different methods of ASR measurement.
- In-situ measured samples were heavily affected by platinum electrodes.
- ASR values of ex-situ measured samples could be related to oxidation.
- The oxidation and chromium volatilization were monitored.

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ABSTRACT

AISI 441 coated with a double layer coating of 10 nm cerium (inner layer) and 630 nm cobalt was investigated and in addition the uncoated material was exposed for comparison. The main purpose of this investigation was the development of a suitable ASR characterization method. The material was exposed to a simulated cathode atmosphere of air with 3% water at 850 °C and the samples were exposed for up to 1500 h. We compared two methods of ASR measurements, an in-situ method where samples were measured with platinum electrodes for longer exposure times and an ex-situ method where pre-oxidized samples were measured for only very short measurement times. It was found that the ASR of ex-situ characterized samples could be linked to the mass gain and the electrical properties could be linked to the evolving microstructure during the different stages of exposure. Both the degradation of the electric performance and the oxygen uptake (mass gain) followed similar trends. After about 1500 h of exposure an ASR value of about 15 mΩcm^2 was reached. The in-situ measured samples suffered from severe corrosion attack during measurement. After only 500 h of exposure already a value of 35 mΩcm^2 was obtained.

1. Introduction

Solid oxide fuel cells are seen as a key element in future energy and heat production. Due to their large versatility they can be used both in stationary, for example CHP applications, but also in mobile applications, such as auxiliary power units. Several fuel cell units need to be stacked to reach sufficient power densities and so-called interconnects are needed connect two adjacent fuel cell elements.

Improvements in electrode and electrolyte performance have led to lower operational temperatures, which allow the use of metallic interconnects [1–3]. There has been extensive research on the development of suitable alloys, which have to have a similar coefficient of thermal expansion (CTE) compared to the ceramic fuel cell elements, a good high temperature stability and that form reasonable electrical conductive oxide scales. Examples of these alloys are Crofer 22 H, Crofer 22 APU, Sanergy HT or ZMG 232 [4–6]. Other alloys that have not been specially developed for fuel cell applications, such as AISI 441 or AISI 430, have also been investigated [1,7–9]. All of the alloys mentioned are ferritic stainless steels that form chromium-containing oxide scales, which protect the steel from rapid oxidation.

With respect to the interconnect one can identify three major factors that are detrimental for the SOFC performance; the oxidation of the steel, the evaporation of chromium and an increasing electrical resistance due to the oxide scale formation.

The oxidation of the interconnect on both the anode and

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cathode side leads during long term operation to a depletion of chromium – which then allows enhanced oxidation and finally leads to mechanical disintegration. Oxidation of the steel can usually be quantified by gravimetry, which is proportional to the oxygen uptake, if no spallation or evaporation processes are involved.

Due to the water vapor present in the cathode atmosphere, the chromium-rich oxide scale evaporates a small amount of chromic species ($CrO_2(OH)_2$), which then react at the cathode/electrolyte/air triple points. This is known as cathode poisoning and is another detrimental factor for the fuel cell performance [10,11]. A relatively new technique for chromium evaporation measurement was developed at Chalmers University of Technology and allows the time-resolved quantification of evaporated chromium for different samples [12].

The growing oxide scale finally leads to an increased electrical resistance across the interconnect. A common way of expressing the electrical resistance is using the term area specific resistance (ASR). This is the cross plane resistivity given in $m\Omega \text{ x } cm^2$, which allows the comparison of different interconnect materials, without additional calculation steps for different oxide scale thicknesses.

Additional coatings are a common way to reduce the above mentioned issues and to improve the interconnect performance with regard to corrosion, chromium evaporation and electrical resistance [13]. The coatings vary in thickness and composition. A compilation of coatings for interconnects can be found in our previous study on improving corrosion properties and mitigating chromium evaporation of AISI 441 by the use of nanometer thick coatings. There it was found that both lifetime and chromium evaporation could be significantly improved by the application of an additional coating of cerium and cobalt [1]. However no data on the ASR evolution was reported, but will be presented in this work.

The characterization of the area specific resistance (ASR) is complicated by a number of issues, in particular contacting. Different methods have been developed, which can be differentiated by the material that is used for contacting the oxide scale. All methods usually have in common that the ASR is considered to be determined by the growing oxide scale and the resistance of the steel itself is neglected. The ASR can be usually expressed as shown in equation (1) [14]:

$$ASR_{Interconnect} = \rho * \tau \tag{1}$$

where ρ is the specific resistivity of the oxide scale and τ is the oxide scale thickness. The ASR is usually given in $m\Omega cm^2$. In case of a double layered oxide scales consisting of an inner chromia layer and an outer spinel layer usually found on SOFC interconnect steels the relationship expands to:

$$ASR_{Interconnect} = \rho_{chromia} * \tau_{chromia} + \rho_{spinel} * \tau_{spinel} \tag{2}$$

Taking into account that the specific resistivity is more or less constant during exposure and in case of a coated interconnect, highly conductive spinels are used as coating material; one can assume that the ASR value is almost directly related to the chromia thickness. Thus the ASR should be proportional to the mass gain of the steel.

The contact materials used for ASR characterization can be classified into noble metals such as platinum, gold or silver, which are not supposed to react or influence the oxidation behavior, and contacts, which are used in solid oxide fuel cell cathodes such as LSM ($La_{1-x}Sr_xMnO_3$) or LSC (LaSrCoO) [9,15–22]. Both have advantages and disadvantages. Noble metals that are not reacting with the oxide material give a more theoretical view of the conductivity evolution, whereas SOFC cathode materials simulate more realistically how the ASR is expected to evolve in a real fuel cell stack. A problem with using noble metals as contact material is often in achieving a reasonable thickness of electrode and therefore metal pastes, which are applied as contacts, have been a common way to apply these electrodes. These pastes often sinter during the initial part of the high temperature exposure, which affects the ASR values [23,24]. In cases where LSM or LSC is used one has also encountered sintering effects in the early stages of exposure, the contact area is undefined, and there is a higher electrode resistance and also contact resistance [15,25]. Additionally interactions between the electrodes with the interconnect steels have been reported [26].

2. Experimental

2.1. Sample preparation

Pre-coated steel sheets with 0.2 mm thickness of AISI 441 (composition given in Table 1) were obtained from Sandvik Materials Technology AB. The sheets were manually cut into coupons of $15 \times 15 \text{ mm}^2$. The coating was applied at Sandvik Materials Technology using an industrially available PVD coating process. Metallic targets were used to produce the double layer coating which consists of an inner coating of 10 nm cerium and an outer layer of 630 nm cobalt. The samples were ultrasonically cleaned in two steps, first in acetone and then in ethanol, and finally the samples were weighed using a Sartorius MC5 scale.

2.2. Exposure

The samples were exposed using the denuder technique and tubular furnaces with a temperature of 850 °C and an absolute humidity of 3% water content were used. The air flow was set to a value of 6 l/min, which is equal to 27 cm/s and which was proven in previous works to be in the flow independent regime of chromium evaporation [12]. Details on the exposure setup can be found in Ref. [1]. Samples were exposed both isothermally (no cool-down until the end of the exposure) and discontinuous (several interruptions with weighing in-between) for up to 1500 h.

2.3. Area specific resistance measurements

We used a new approach to produce area-defined electrodes of platinum to measure the ASR. A sputter mask of $10 \times 10 \text{ mm}^2$ was placed on a pre-oxidized sample, and the sample was then sputtered with platinum for 10 min using a Quorum 150 sputter coater and a sputter current of 60 mA. This procedure was then repeated for the reverse-side of the sample. The sputtering step was used in order to produce electrodes with a defined area and to avoid direct contact of the platinum paste with the sample surface. After sputtering, the electrodes were re-painted with platinum paste (Metalor 6082) using a fine brush. To remove the binder from the platinum paint, the samples were fired at 850 °C in air with a peak time of 10 min. To investigate the time-dependent evolution of the ASR different pre-oxidation times up to 1500 h were used. Additionally a few samples were measured after a pre-oxidation time of only 60 min for up to 500 h – below referred as in-situ samples.

A Probostat (NorECs, Norway) test cell, placed in a tubular

Table 1
Batch-specific values provided by the manufacturer, given in wt. %.

	Fe	Cr	C	Mn	Si	S	P	Ni	Nb	Ti
Wt. %	Bal.	17.83	0.012	0.26	0.55	0.002	0.024	0.13	0.48	0.14