ABSTRACT

In planar SOFC stacks with ferritic interconnects and anode substrate-supported SOFC cells degradation is still too high for stationary applications. Determination of the sources of this degradation is difficult due to the complexity of the stacks. Methods for separating detrimental influences under conditions closely resembling stack operation and environment must be developed. Using an inert cell housing with exchangeable inserts at the electrodes provides an opportunity to selectively place stack materials close to the cathode. Results from these measurements show a clear poisoning of the cathode by chromia from the ferritic steel. Degradation rates above 20% in 1000 hours are observed for Crofer22APU-1st (first commercial batch) despite the formation of chromium manganese spinel oxide layer on the surface of the steel that reduces the release of chromium species from the steel. Coating the steel with contact layer material on average reduces the degradation rate close to 0% for the first 600 hours. After prolonged operation for 1800 hours a noticeable degradation can be observed for cells exposed to coated steel. The mechanism of the chromia retention by the contact layer is not yet clear.

INTRODUCTION

One of the predominant problems in planar SOFC stacks with metallic interconnect is the durability. The degradation of the stack potential is in general still too high for prolonged operation over more than 40,000 hours (1,2). This degradation phenomenon is frequently attributed to one or more processes, e.g. chromia poisoning, oxidation of metals, changes in microstructures of electrodes, etc. A direct correlation between the degradation and these processes is difficult to establish. Therefore a method for establishing direct relation between different sources of degradation and the electrochemical performance of a cell in a stack-related environment is needed (2). Frequently measurements of materials properties yield results that are difficult to correlate with results obtained from stacks due to complex interactions of all the materials in the system. The techniques applied for separation of detrimental contributions should therefore closely resemble the operation of stacks i.e. it should at least incorporate the electrochemical processes.

One of the established sources of degradation in stacks is the poisoning of the cathode by chromium(VI) species evaporating from the metal parts in the stacks (3,4). This effect can be blocked by the use of protective layers. Examples of these protective layers can be
found in literature e.g. plasma-sprayed lanthanum chromite on Ducalloy (5). Deposition of these layers introduces additional production steps and thus increases the manufacturing costs of SOFC stacks. Therefore attempts are made to provide these protective layers in situ. One example is the development of ferritic steel forming a spinel oxide layer (6) or the wet coating of such steels with ceramics (7).

Measurements on stacks also indicated that the cathodic contact layer can play a role in the protection of the cathode from chromia poisoning. This effect was studied in more detail with a setup allowing the introduction of materials used in stacks close to the cathode of a SOFC single cell (2). The data published on the degradation of anode substrate-supported SOFC single cells showed a remarkable effect of a lanthanum cobaltite layer deposited on steel 1.4742 on the degradation rates of a single cell placed near this material combination. This effect was observed by placing coated and non-coated pieces of metal in close vicinity of an operating cathode and monitoring the cell voltage. The materials 1.4742 and lanthanum cobaltite are, however, no longer interesting for stack construction. The previously mentioned technique of placing metal parts close to an operating cathode is used to test the chromia poisoning of the cathode by currently used materials for stack construction.

By combining the results of these experiments with actual stack measurements, measurements on chromia evaporation (3), corrosion experiments and microstructural analysis, a deeper understanding of the processes leading to stack degradation may be obtained.

**EXPERIMENTAL PROCEDURES**

The experiments are conducted in a furnace comprising eight single cell test housings. The housing for cells of 5 x 5 cm² is constructed completely of aluminum oxide. A platinum and a nickel mesh current collector is used on the cathode and anode side of the single cell, respectively. The effective electro-chemical surface area is 16 cm². Sealing of the cell is obtained using a gold wire gasket. The current collectors and the gasket are pressed on the cell using additional weights. On both sides of the cell are removable alumina plates with gas channels (see schematic drawing and photograph in Figure 1). When using electrically conducting inserts, e.g. steel (2), the current can optionally be collected using a mesh or directly from the insert. This arrangement allows distinguishing indirect influences such as poisoning by volatile species evaporating from the insert from direct influences such as an increase in resistance from oxide scale growth. By systematically varying the materials used as inserts and coatings of the inserts, e.g. contact layers, the influences of the different materials and layers in such assemblies on the degradation can be separated. Some restrictions have to be kept in mind though. Because of the use of a gold gasket there is a high probability of small leakage between the gas compartments. This means that especially the humidity in the air compartment is difficult to control. As the humidity can have a major effect on the chromia evaporation which is the focus of this study, the results of the experiments were evaluated against this background.

The testing procedure consists of a heating program comparable to the program used for stacks. During heating the cell is flushed with argon and air on the fuel and air side,
respectively. The heating is followed by a slow reduction of the nickel oxide in the substrate. This is accomplished by gradually increasing the hydrogen partial pressure in the anode gas. After reduction the cell is operated under 1 nl/min of hydrogen with 3% water vapor on the anode side and 1 nl/min of dry air on the cathode side and current-voltage curves at different temperatures are measured. Subsequently the cell is brought to a temperature of 1073K (800°C) and a current of 5 A (0.3 A/cm²) is applied to the cell. The cell voltage is then monitored over a period of at least 500 hours. One series of measurements was conducted for 1500 hours.

RESULTS

The results of the experiments are grouped into three categories: intrinsic cell degradation, metal induced cell degradation due to metal presence at the cathode and moderated insert induced cell degradation due to contact layer coated metal near the cathode.
Intrinsic Cell Degradation

To establish a base line for the degradation effects observed in SOFC stacks, on several occasions measurements of single cells with alumina inserts in the housings were conducted over a period of several hundred hours. These measurements were conducted in parallel to the experiments with metal inserts insuring comparable conditions for the cells. The results of these measurements are presented in Figure 2. The cells operated at different cell voltages. This is due to differences in the quality of the electrical contact between the cell and the current collectors. Over time the performance of the cells improved due to changes in the microstructure of the electrodes, most likely due to changes of the surface morphology of the grains. Apart from the absolute voltage values the behavior of the cells is similar. After a rapid increase in cell voltage during the first few hours under current load, the cell voltage slowly continues to increase over a period of 200 hours. After this period the cells run at a constant level. Linear least square fit analysis of the data shows a gradual change in cell voltage over the remaining hours of operation. This change varies between -1.2% to +0.8% in 1000 hours. These data are in good agreement with data published previously on long term operation of anode-supported SOFCs in an inert test housing. Here also cell degradation of smaller then 1% in 1000 hours was reported (2). On average the degradation of the cell voltage is close to zero. This makes these anode substrate-supported SOFCs suitable for use in stacks for stationary applications.

Metal Induced Cell Degradation

In these experiments the alumina insert at the cathode side of the cell was replaced by an insert machined from different steel compositions. The curve for steel 1.4742 was published earlier (2) and is added for comparison. The other three curves are all for JS3-type steel. JS3/KTN is a batch of steel produced under laboratory conditions.
Crofer22APU-1st is the first batch of steel produced on industrial scale. The differences in composition are given in (8). All samples designated Crofer22APU-1st are produced from the same piece of sheet metal.

The behavior of the SOFCs with a steel insert close to the cathode is markedly different from the behavior of cells in an inert surrounding as can be seen in Figure 3 and Figure 4.

**Figure 3.** Constant current measurements on single cells with metal inserts close to the cathode. V: Crofer22APU-1st/1; Δ: Crofer22APU-1st/2; □: JS3/KTN; ○: steel 1.4742

**Figure 4.** Constant current measurements on single cells with metal inserts close to the cathode. V: Crofer22APU-1st/1; Δ: Crofer22APU-1st/2; □: JS3/KTN; ○: steel 1.4742. The drawn line indicates a degradation rate of 21% in 1000 hours.
These figures show the same data but on different time scales. Instead of a rapid increase in cell voltage during the first few hours, a rapid decrease in cell voltage can be observed during the first 24 hours. After this initial decrease the cell voltage starts to decrease with a constant rate for 3 of the 4 samples. The sample with steel 1.4742 shows a degradation rate of 6% in 1000 hours. The samples Crofer22APU-1st/2 and JS3/KTN show a rate of degradation of 29% and 22% in 1000 hours, respectively. The degradation rate of sample Crofer22APU-1st/1 after the first 24 hours is clearly lower. The curve shown is representative for a series of 4 measurements all showing a similarly low degradation rate between 4% and 7% in 1000 hours over a period of about 300 hours. After this period the degradation rate of these cells slowly increases to a value of 21% in 1000 hours (see Figure 4).

**Moderated Insert Induced Cell Degradation**

This group of measurements is conducted using metal inserts from Crofer22APU-1st as previously described but coated with a cobalt oxide containing contact layer material. During these measurements again a cell voltage drop during the first 24 hours can be observed for most samples (Figure 5). After this time the samples all come to a constant degradation rate between 2.5% and -2.5% in 1000 hours for a period of about 400 hours. These rates vary somewhat more than the rates for the single cells. For one series of cells the experiments were conducted over a longer period. In this experiment the degradation stayed well below 1% in 1000 hours up to 1000 hours of constant current load. Continued operation showed a slow increase of the cell voltage degradation rate over the subsequent 800 hours of operation.

![Figure 5. Constant current measurements on single cells with Crofer22APU-1st inserts coated with contact layer material close to the cathode.](image)

**DISCUSSION**

The measurements on single cells in an inert surrounding clearly show a degradation of the cells lower than 1% in 1000 hours. This degradation increases dramatically in the
presence of chromium-containing steel near the cathode. Cells showing this kind of rapid degradation were cut and the cross section was studied with a scanning electron microscope with a wave dispersive analyzer. Large amounts of chromium could be detected in the electrode close to the electrode/electrolyte interface (as left picture in Figure 6). Furthermore crystals of chromium manganese oxide could be found in the area with high chromia concentration. This is in agreement with previous observations (4,5) relating chromia deposition at the three phase boundary to high degradation rates of the cell voltage during electric load.

Cross sections from samples operated less than 600 hours with the coated steel inserts showed no detectable amounts of chromia in the electrode and look the same as Figure 6, right picture. Unfortunately the analysis of the sample that was operated for 1800 hours is still pending. Analysis of the coated steel inserts showed a distinct reaction layer between the steel and the coating. This layer contains high amounts of chromium and cobalt coming from the contact layer. Apparently this reaction layer is effectively blocking the evaporation of chromia from the steel thus preventing a poisoning of the cathode. Whether the layer is functioning as a getter absorbing the evaporating chromium species or the reaction layer is providing a diffusion barrier can not yet be determined. The increase in degradation rate observed during the experiment with a coated steel insert over 1800 hours indicates that the contact layer material is functioning as a getter. Analysis of the steel plate from this experiment will provide more information on the blocking mechanism.

Figure 6. Cathode composite layer of a cell operated for 6000 h in a stack and a cell after short-term cell testing in an alumina housing. The dark gray areas leading to the densification of the left composite layer are strongly enriched in chromium.

CONCLUSIONS

The degradation of anode substrate-supported single cells well below 1% in 1000 hours of operation is sufficient for long term operation of fuel cells.

The use of unprotected chromium steels in stack construction leads to severe degradation of the cell voltage due to chromia poisoning of the cathode.

Use of cathode contact layers can block most of the chromia evaporation resulting in low degradation rates for the cell voltage. Important is, that all hot air exposed steel surfaces must be covered with the contact layer material.
ACKNOWLEDGEMENT

The authors wish to thank all members of the Jülich SOFC team for their contributions. Special thanks go to Dr. Egbert Wessel and Dr. Doris Sebold for performing the electron microscope analysis.

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