LONG TERM STABILITY OF YTTRIA AND SCANDIA DOPED ZIRCONIA ELECTROLYTES

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ABSTRACT

The decrease of the intrinsic electrical conductivity of various yttria and scandia doped zirconia electrolyte tapes was examined during long time exposure at 950 °C by four-point dc measurements. Different sintering profiles were applied to determine influence of phase composition and microstructure on degradation rate. The investigated specimen showed a degradation rate of 16 -38 % during the first 1000 hours, whereas the degradation rate decreased exponentially by time. For the 8YSZ specimen it was found that samples sintered below 1500 °C exhibited a significantly higher degradation than the specimen sintered at higher temperature. Degradation of 3YSZ specimen was somewhat lower and was accompanied with an increase of the tetragonal phase at expense of the cubic phase. In case of 4SSZ only slight change of the conductivity was observed after 2000 h of annealing. Although samples sintered according to a rate controlled sintering profile showed a slightly higher conductivity than conventionally sintered samples not much difference in degradation behavior was observed.

INTRODUCTION

SOFC single cells are exposed to various types of degradation mechanisms during operation. The decrease of the intrinsic electrolyte conductivity is of importance for electrolyte supported single cells. Various investigations on the long term stability of zirconia based electrolytes has been carried out in the past by many researchers (1-4). It was found that most zirconia specimen exhibited severe degradation during long time exposition at high temperatures.

In this work the electrical conductivity of various zirconia based electrolyte substrates doped with yttria or scandia was monitored at 950 °C as a function of time for up to 3500 hours. In contradiction to other researches thin electrolytes tapes, that are used for electrolyte supported single cells, were investigated and not bulk samples. Different sintering profiles were applied to determine influence of phase composition and microstructure on the degradation rate.

EXPERIMENTAL

Electrolyte tapes from Nippon Shokubai and other suppliers with a thickness between 80 and 200 μm were investigated. The zirconia samples were doped with 8 mol% (8YSZ) and...
3 mol% (3YSZ) yttria and 4 mol% scandia (4SSZ), respectively. Different sintering profiles were applied to determine influence of phase composition and microstructure on degradation rate. Maximum sintering temperature and profile type — constant heating rate (RCS) — were varied. The electrical conductivity of different specimens with a width of about 10 mm and 50 mm in length was determined in air by four-point dc measurements at 950 °C. The applied current density between 120 and 290 mA/cm² — depending on sample geometry — was held constant between 1000 and 3500 hours. The samples were contacted by platinum paste and platinum wires.

X-ray analysis was carried out before and after long time exposures with a Siemens D5000 diffractometer in the 2θ-range 20-80° with a step size of 0.0357° and a counting time of 8 s. The phase composition of the samples was evaluated by the Rietveld method (6).

RESULTS AND DISCUSSION

In fig. 1 the decrease of the electrical conductivity $\sigma$ of different 8YSZ electrolytes is shown. A decrease of the conductivity which could be described by an exponential law was observed. The numbers indicate the degradation rate after 1000 h and 2700 h, respectively. All specimens exhibited a degradation rate of more than 23% during the first 1000 hours and the degradation continued for the next 1700 hours at a high rate. Although the specimen sintered at temperatures below 1500 °C had a higher conductivity at the beginning than the specimen sintered at higher temperatures, they exhibited much more degradation during long time operation. However, no difference in phase composition was detectable. XRD analysis revealed that all 8YSZ samples were cubic with a little amount of monoclinic phase (<1%) which disappeared after long time exposure. It is assumed that the higher degradation rate of the low sintered specimen is attributed to the larger amount of grain boundaries due to their smaller grain size.

The 3YSZ and 4SSZ samples indicated similar behavior than the 8YSZ specimen. The exponential decay of the electrical conductivity can be seen in fig. 2. However, the degra-
Figure 2. Electrical conductivity decrease of 3YSZ and 4SSZ electrolyte tapes sintered with various temperature profiles.

Degradation rate of the 3YSZ during the first 1000 hours was only 18% in comparison to the 8YSZ samples. The sample 3YSZ-b had a cubic phase component of 50 vol% and therefore a higher conductivity than the other 3YSZ samples, but the degradation rate was comparable.

Phase analysis indicated an increase of the tetragonal phase during annealing at expense of the cubic and monoclinic phase for the 3YSZ samples. Details can be seen in Table I.

Table I. Phase composition of the various 3YSZ electrolyte tapes as a function of time (t: tetragonal; c: cubic; m: monoclinic).

| sample                | phase | 0 h  | 1000 h | 3500 h |
|-----------------------|-------|------|--------|--------|
| 1430 °C (NS<sup>a</sup>) | t     | 83%  | 86%    | 88%    |
|                       | c     | 16%  | 14%    | 13%    |
|                       | m     | 2%   | 0%     | 0%     |
| RCS<sup>b</sup> 1300 °C (NS) | t     | 87%  | 92%    | -      |
|                       | c     | 14%  | 9%     | -      |
|                       | m     | 0%   | 0%     | -      |

<sup>a</sup> rate controlled sintering  
<sup>b</sup> from Nippon Shokubai

Degradation rate of the 4SSZ specimen during the first 1000 hours was comparable to the 8YSZ samples. However, the time constant of the exponential decay was smaller so that only slight change of the conductivity was observed after 2000 h of annealing. XRD analysis revealed that the 4SSZ specimen consisted solely of the tetragonal phase.

In both cases, 3YSZ and 4SSZ, not much difference in degradation behavior was observed between the samples sintered according to a RCS profile and the conventionally sintered samples. However, the RCS samples had a slightly higher conductivity.

The conductivity values of all investigated zirconia samples after different exposure times
Table II. Electrical conductivity in S/m of various zirconia electrolyte tapes as a function of time.

| sample          | 0 h  | 500 h | 1000 h | 1500 h | 2000 h | 2500 h | 3000 h | 3500 h |
|-----------------|------|-------|--------|--------|--------|--------|--------|--------|
| 8YSZ            |      |       |        |        |        |        |        |        |
| RCS 1350 °C     | 16.1 | 12.4  | 10.8   | –      | –      | –      | –      | –      |
| RCS 1500 °C     | 16.0 | 13.5  | 12.3   | 11.4   | 10.7   | 10.1   | –      | –      |
| 1550 °C         | 15.6 | 13.2  | 11.9   | 10.9   | 10.2   | 9.7    | –      | –      |
| 1430 °C (8YSZ-b) | 16.5 | 11.7  | 10.3   | –      | –      | –      | –      | –      |
| 3YSZ            |      |       |        |        |        |        |        |        |
| 1430 °C (NS)    | 4.5  | 4.0   | 3.8    | 3.7    | 3.6    | 3.5    | 3.5    | 3.4    |
| RCS 1300 °C (NS)| 4.9  | 7.5   | 4.0    | –      | –      | –      | –      | –      |
| 1400 °C (3YSZ-b) | 6.2  | 5.4   | 5.0    | 4.8    | 4.7    | –      | –      | –      |
| 4SSZ            |      |       |        |        |        |        |        |        |
| 1350 °C (NS)    | 9.3  | 7.5   | 7.2    | 6.9    | 6.8    | 6.8    | 6.7    | 6.6    |
| RCS 1300 °C (NS)| 9.6  | 7.6   | 7.3    | –      | –      | –      | –      | –      |

* 50 vol % cubic phase

are given in table II.

CONCLUSIONS

All investigated specimen showed high degradation of the electrical conductivity during long term exposure at 950 °C, whereas the decay of the electrical conductivity was described by an exponential law. Among the various specimen degradation rate of the 8YSZ specimen was the highest especially of the samples sintered below 1500 °C. An increase of the tetragonal phase during annealing at expense of the cubic and monoclinic phase was detected for the 3YSZ samples. The 3YSZ and 4SSZ samples sintered according to a RCS profile had slightly higher conductivity values than conventionally sintered specimen, but degradation rate was similar. It is remarkable that the conductivity of the 3YSZ and 4SSZ samples decreased mainly during the first 2000 hours and only slight decay of the conductivity was noticed afterward.

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