Long Term Stability of Yttria and Scandia Doped Zirconia Electrolytes

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SOFC single cells are exposed to various types of degradation mechanisms during operation. The degradation of intrinsic electrolyte conductivity is of importance for electrolyte supported single cells. Therefore, the electrical conductivity of various zirconia based electrolyte substrates was monitored at 950 °C as a function of time.

Electrolyte tapes from various suppliers (NS stands for Nippon Shokubai) with a thickness between 80 and 200 µm were investigated. The zirconia based 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/rate controlled sintering (RCS) – were varied.

The electrical conductivity σ of different specimen with a width of about 10 mm and 50 mm in length was determined in air by four-point dc measurements. The applied current density between 120 and 290 mA/cm^2 – depending on sample geometry – was held constant between 1000 and 3500 hours. X-ray analysis (XRD) was carried out before and after long time exposures to quantify phase composition by the Rietfeld method.

In fig.1 the conductivity decrease of different 8YSZ electrolytes is shown. The numbers indicate the degradation rate after 1000 h and 2700 h, respectively. All specimen exhibited a degradation rate of more than 23 % during the first 1000 hours and degradation continued for the next 1500 hours at a high rate. The specimen sintered at temperatures of 1500 °C and higher showed less degradation in comparison to the specimen sintered at lower temperatures. However, no change in phase composition was detectable. All 8YSZ samples consisted solely of the cubic phase.

The degradation rate of the 3YSZ and 4SSZ samples (fig.2) during the first 1000 hours was 18 % and 24 % respectively. However, a strong decrease of the degradation rate was observed, which came to a rate of 1.7 and 1 % for the last 1000 hours shown in fig.2 for the 3YSZ and 4SSZ samples, respectively. Phase analysis indicated an increase of the tetragonal phase at expense of the cubic phase. The sample 3YSZ-b was not fully tetragonal stabilised and consisted of 50 % cubic phase. However, degradation rate was comparable to the tetragonal stabilised specimen. In table 1 are the conductivity values for the various samples after different exposure times listed.

All investigated specimen showed high degradation of the electrical conductivity during long term exposure at 950 °C, whereas the degradation rate decreased by time. Samples sintered according to a RCS profile had slightly higher conductivity values, but degradation was similar. It is remarkable that the conductivity of the 3YSZ and 4SSZ samples decreased only during the first 2000 hours and remained then nearly stable.

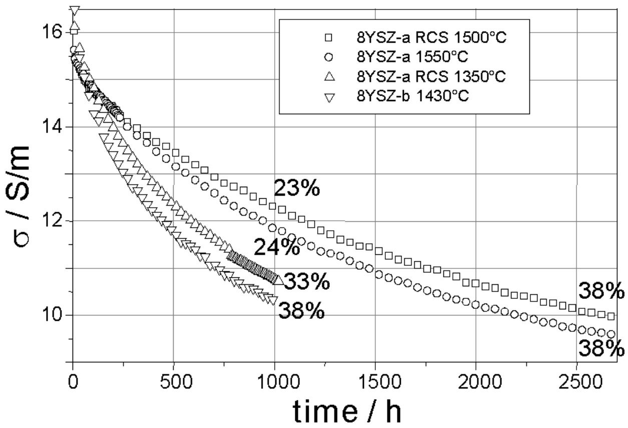

Fig. 1: *Electrical conductivity decrease of 8YSZ electrolyte tapes sintered with various temperature profiles.*

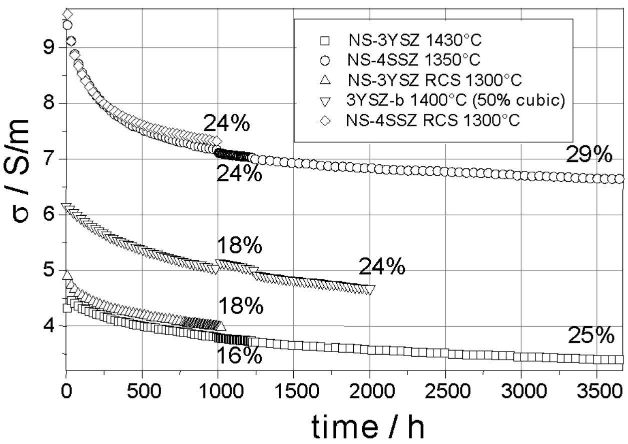

Fig. 2: *Electrical conductivity decrease of 3YSZ and 4SSZ electrolyte tapes sintered with various temperature profiles.*

Table 1: Electrical conductivity in S/m of various zirconia tapes as a function of time.

sample	0 h	1000 h	2000 h	3000 h	3500 h
8YSZ					
RCS 1350 °C	16.1	10.8	–	–	–
RCS 1500 °C	16.0	12.3	10.7	–	–
1550 °C	15.6	11.9	10.2	–	–
1430 °C (8YSZ-b)	16.5	10.3	–	–	–
3YSZ					
1430 °C (NS)	4.5	3.8	3.6	3.5	3.4
RCS 1300 °C (NS)	4.9	4.0	–	–	–
1400 °C (3YSZ-b, 50 % cubic)	6.2	5.0	4.7	–	–
4SSZ					
1350 °C (NS)	9.3	7.2	6.8	6.7	6.6
RCS 1300 °C (NS)	9.6	7.3	–	–	–