LOW TEMPERATURE DENSIFICATION OF SOFC ELECTROLYTES USING MANGANESE OXIDE AND BORON OXIDE

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ABSTRACT

To reduce the sintering temperature of yttria-stabilized zirconia (8YSZ) the influence of the addition of a pre-reacted mixture from manganese oxide and boron oxide on the densification behaviour was analyzed. The experiments were carried out on pressed pellets as well as on tubular SOFCs from Siemens Fuel Cells. Different sintering aid contents were investigated using sintering temperatures from 1200 up to 1400 °C and a dwelling time of 5 h, respectively. With all sintering aid contents, a distinct increase in the density of the pellets could be observed. In contrast to that, the addition of low amounts of the sintering aid in the electrolyte coatings results in no noticeable increase in the density. Additions of higher amounts of sintering aid leads to an increase of the density after comparable sintering. No evidence of an undesired compaction of the cathode leading to a low polarization in the cathode was observed.

INTRODUCTION

In solid oxide fuel cells, yttria-stabilized zirconia is the commonly used electrolyte material. Besides good ionic conductivity, the gas tightness of this membrane is the most important property. To ensure gas tightness of the electrolyte, sintering is normally carried out at temperatures of 1500°C or higher (1,2). Reducing the sintering temperature leads to porosity in the electrolyte, which results in leakage of fuel or air lowering the cell efficiency or complete destruction of the cell (3). In contrast to the high sintering temperature of the electrolyte, the cathode tolerates only a maximum temperature of about 1200°C. This is due to the enhanced sintering activity of this perovskite material leading to a drastic increase in particle size (coarse microstructure) and thus in a reduced amount of triple phase boundary area (tpb; atmosphere/electrolyte/cathode) and subsequently in decreased cell efficiency (4). To overcome this problem, two possible variations can be chosen. The first possibility is to enhance the cathode materials either by developing new materials or by using sintering inhibitors like ceria. The second way is to reduce the sintering temperature of the electrolyte. Lower sintering temperatures combined with a fully densified electrolyte could be realized either by using nanosized starting materials or by the addition of sintering aids.

In the literature, different oxides like Al2O3 (5,6), NiO (7), Bi2O3 (8), SiO2 (9-11), TiO2 (2,10) and Fe2O3 (8,12) are proposed as sintering aids for zirconia stabilized with CaO,
Sc$_2$O$_3$ or Y$_2$O$_3$. However, most of these sintering additives did not only lower the sintering temperature, but they have also a negative influence on the electrochemical capacity of the cell. While silica enormously increases the resistivity of YSZ at low operating temperatures, titania together with CSZ as well as iron and bismuth oxide together with YSZ increases the resistivity, too. Due to this the use of these sintering additives is prohibitive. Contrary to the former ones, low amounts of alumina seem to be a good sintering additive without any negative influence on the cell performance.

In contrast to the oxide sintering additives, boron nitride as a non-oxide additive seems to be a promising candidate (3) for lowering the sintering temperature, but the high evaporation rate at temperatures above 1000°C causes additional efforts during the sintering of the samples. Ongoing investigations with an advanced pre-treated sintering aid based on a pre-reacted mixture from boron oxide and manganese oxide are presented in this paper.

**EXPERIMENTAL**

**Substrates**

For the experiments, tubular SOFCs from Siemens Westinghouse (Pittsburgh, USA), made by a newly released patent (13), were used. The coatings of the interlayer composed of a mixture of LCM and YSZ were prepared by wet powder spraying technique (3,14), which is an established technology in coating planar SOFCs. The ceramic interconnect was masked by an adhesive strip to avoid coating with undesired material. After applying the interlayer and subsequent drying, the samples were sintered at moderate temperatures > 1000°C, resulting in a well defined porous microstructure of the interlayer.

**Sintering Aid**

As sintering aid, a pre-reacted mixture from manganese oxide and boron oxide was used. Starting from boric acid a thermal dehydration reaction was conducted in a first step to obtain water free boron oxide. In a second step, this boron oxide was directly pre-reacted at 1000°C for 5 h with the stoichiometric amount of manganese oxide. To avoid evaporation of boron oxide leading to a non-stoichiometric composition of the sintering aid, the reaction was conducted in a closed alumina crucible. After milling, the phase content of the material was examined by X-ray diffraction measurements. Besides the two major phases Mn$_2$O(BO$_3$) and Mn(BO$_2$)$_2$ no other phases were observed within the detection limit. The absence of minor phases like manganese oxide or boron oxide showed that the reaction was complete and that the loss of boron due to evaporation was inhibited to a greatly possible extent.

**Suspension**

Suspensions for the coating experiments were prepared by using fully yttria-stabilized zirconia from Tosoh Company pre-calcined at 1240°C for 3 h, dispersed in ethanol and PEI (Polyethylemimin) as dispersing aid and 3, 5 or 10 wt% sintering aid, respectively. After a combined milling and mixing step the particle size of the suspensions were measured using a laser granulometer. All suspensions show an identical bimodal grain size distribution with d$_{50}$ values in the range of 600 nm.
Coatings and Pellets

Coating of the electrolyte layer was also done by wet powder spraying. For an optimal green density of the layers, coating parameters like deposition distance, nozzle size, spray pressure and velocity of the spraying unit used were according to previous investigations (4). The electrolyte layer was deposited as a twin coating, with a sintering additive free sublayer and a top layer doped with the pre-reacted mixture from manganese oxide and boron oxide. After drying, the sintering was conducted at 1200, 1250, 1300, 1350 and 1400°C with a dwell time of 5 h, respectively. Until 700°C, the heating-up was at a rate of 360 K/h; above this, the rate was increased to 1800 K/h. The cooling rate was determined by the furnace characteristics. To avoid evaporation of boron oxide, sintering was conducted in covered alumina crucibles. The overall thickness of the electrolyte layer was in the range of 35 to 40 µm after sintering, according to measurements on polished cross-sections. The leak rates were determined by window leak test.

For the preparation of pellets, the suspensions were dried in a cabinet desiccator at 110°C. After milling, pellets with a diameter of 8 mm and a height of 1.5 mm were prepared with a pressing mould at a final pressure of 25 kN. The green density of all pellets was about 3 g/cm³. For sintering, analogue sintering parameters as for the electrolyte layers were used. The theoretical density of the sintered samples was estimated by Archimedes method.

RESULTS AND DISCUSSION

Sintered Pellets

As can be seen in figure 1, samples without a sintering aid first show an increase in the theoretical density in the temperature range of 1100 to 1150°C. After a slight increase, a density of 88% of the theoretical density is reached (fig. 1). This behaviour of the densification could be explained as a typical diffusion controlled sintering mechanism, which is typical for a solid state sintering process. In contrast to pellets without any sintering aid, samples with 3, 5 or 10 wt% additive show a beginning of the densification between 1000 and 1050°C. At temperatures in the range of 1050 and 1100°C, all pellets independent of the amount of sintering aid exhibit a scarped increase in the density. Any further increase in temperature does not lead to further compaction of the samples. Nevertheless, the maximal density of these samples in the range of 75 up to 80% of the theoretical density is considerably lower than the density of samples without any additive. The lower density as well as the scarped increase could probably be explained by the formation of a liquid phase.

The assumption of a densification at lower temperatures caused by a liquid phase is supported by differential thermal analysis and thermogravimetric measurements shown in figure 2. Starting with non-reacted manganese and boron oxide, the endothermic reactions combined with the weight losses at 590, 915 and 1190°C can be attributed to changes of the oxidation state or to the phase content. The endothermic peak at 1125°C or at 1120°C in case of the pre-reacted mixture can be associated with the melting point of a liquid phase. This is in good agreement with a dilatometric measurement showing a softening of the sample at a comparable temperature (not shown here).
Theoretical density of pellets sintered at different temperatures with a dwell time of 5 h containing 3, 5 or 10 wt% sintering aid, respectively.

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For investigations on the phase stability of fully yttria-stabilized zirconia in the presence of the sintering aid, pellets sintered at 1350°C for 5 h were crushed and milled in an agate mortar. X-ray diffraction measurements revealed no change in the phase content of the stabilized zirconia for additive contents of 3 and 5 wt%. In contrast to that, pellets with 10 wt% show the occurrence of a new phase YBO₃, due to destabilisation of yttria in the zirconia lattice.
Sintered Coatings

After coating and sintering of the tubular SOFC, a first characterization was conducted by measuring the permeation of air through the sample (table I). Comparing the leak rates for samples with 3 wt% sintering aid a lowering of the leak rate could be observed with an increasing temperature. Lowest and therefore best values were obtained for samples sintered at 1400°C, but nevertheless the internal threshold value of $2.3 \times 10^{-4}$ mbar l/s cm$^2$ was not achieved. Better values were obtained for samples with 5 or 10 wt% additive. In contrast to samples with 3 wt% all samples sintered at $\geq 1350^\circ C$ showed leak rates in the range of the threshold value, independent of the amount of sintering additive. The slight increase of the leak rate for samples with 10 wt% sintered at 1400°C can be attributed to a decomposition of the sintering aid combined with an evaporation of boron oxide leading to a higher porosity in the electrolyte layer (fig. 4).

Table I. Average permeation values from three single measurements of samples with 3, 5 or 10 wt% sintering additive sintered at temperatures in the range of 1200 to 1400°C for 5 h.

| sintering aid | temperature | 1200°C | 1250°C | 1300°C | 1350°C | 1400°C |
|---------------|-------------|--------|--------|--------|--------|--------|
| 3 wt%         |             | 2.82   | 1.15   | 1.34*10^{-2} | 2.30*10^{-3} | 4.69*10^{-3} |
|               |             | 3.06   | 1.66   | 3.61*10^{-3} | 8.41*10^{-3} | 2.08*10^{-3} |
| 5 wt%         |             | 2.87   | 3.15*10^{-2} | 1.70*10^{-2} | 1.52*10^{-4} | 3.50*10^{-4} |
|               |             | 2.79   | 3.51*10^{-3} | 3.05*10^{-4} | 1.76*10^{-4} | 1.76*10^{-4} |
| 10 wt%        |             | 2.25   | 7.42*10^{-1} | 2.05*10^{-2} | 2.83*10^{-4} | 2.12*10^{-2} |
|               |             | 2.91   | 7.15*10^{-1} | 2.38*10^{-4} | 4.38*10^{-4} | 3.22*10^{-2} |
Figure 4. Leak rate of samples with 3, 5 or 10 wt% sintering aid sintered at different temperatures. (Lines are guides for the eyes).

Figure 5. Optical microscopy images of polished cross sections of samples sintered at 1350°C for 5 h showing cathode, interlayer and electrolyte. (top left: without sintering aid; top right: 3 wt%; bottom left: 5 wt%; bottom right: 10 wt%)

Characteristic cross sections of all samples with none, 3, 5 and 10 wt% sintering aid are shown in figure 5. Identical in all images is the cathode with the coarser microstructure which is coated with the interlayer with a thickness of about 10 to 20 μm followed by the
electrolyte with an overall thickness of 40 μm. In case of samples without any sintering aid or with 3 wt%, the interlayer as well as the electrolyte layer exhibits always a highly porous microstructure, even after sintering at 1400°C for 5 h. A fully densified electrolyte layer could be observed for samples with 5 or 10 wt% sintering aid sintered at temperatures above 1300°C. The dense microstructure is in good agreement with the permeation rates measured on these tubes. While samples with 5 wt% exhibit a porous interlayer microstructure like samples without or with 3 wt%, tubes with 10 wt% show a densification of the interlayer structure. Presumably this is caused by the decomposition of the sintering aid and evaporation of the boron species. After migration into the interlayer the boron species reacts with the manganese oxide from the perovskite forming an active liquid phase, which supports the densification of the interlayer itself. In contrast to samples with 5 and 10 wt% sintered above 1300°C, tubes sintered below 1300°C show a microstructure of the electrolyte and of the interlayer comparable to samples without or with only 3 wt%.

CONCLUSIONS

The influence of a pre-reacted mixture of manganese oxide and boron oxide as a sintering additive on the densification behaviour of fully yttria-stabilized zirconia has been investigated. Experiments carried out on pressed pellets yielded that the densification of the 8YSZ at temperatures in the range of 1050 and 1100°C is caused by the formation of a liquid phase leading to a scarped increase in density. In contrast to that, addition of 3 wt% sintering aid in coatings on tubular substrates results in no noticeable increase in density or decrease in permeation. This discrepancy in the sintering behaviour could be explained by the different green densities. In case of the pellets the amount of liquid phase is high enough to wet the grain boundaries, while in coatings the amount of the active phase is too low to fill the larger space between the single grains. A complete wetting of the grain boundaries, which is essential for the densification, is not reached. Additions of higher amounts of the sintering additive fulfill this requirement. The beginning of densification of the microstructure of the electrolyte could be observed. Best results with gas permeation rates in the range of the internal threshold value of 2.3 mbar l /s cm² were obtained for these samples. An undesired compaction of the interlayer microstructure was only seen in the case of 10 wt% sintering additive. Nevertheless, an electrochemical characterization of these samples, to investigate the influence of sintering aid and possible changes in the interlayer, is still underway.

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