DENSIFICATION OF SOFC YTTRIA-STABILIZED ZIRCONIA ELECTROLYTES THROUGH ADDITION OF SINTERING ADDITIVES

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ABSTRACT
The use of sintering additives for fully yttria-stabilized zirconia (8YSZ) was investigated in order to reduce the sintering temperature. Both state-of-the-art SOFC systems, i.e. the tubular Siemens Westinghouse design and the planar anode-supported system, were electrolyte-coated by wet chemical methods (e.g. vacuum slip casting and wet powder spraying) with different sintering aids. For the planar system, alumina was used while in the tubular system boron nitride was investigated. The addition of low amounts of alumina (< 2%) resulted in either better gas tightness of the electrolyte sintered at 1400°C or in comparable gas tightness (in comparison to the normally used 8YSZ without additions) at lower sintering temperatures. The performance of single cells is enhanced by addition of alumina for all temperatures measured (750-900°C). For the tubular system low amounts of boron nitride (< 2.5%) led to a strong decrease in the sintering temperature necessary to reach gas tightness (<1300°C). The reaction mechanism for enhanced densification of both sintering experiments was examined.

INTRODUCTION
Yttria-stabilized zirconia is a commonly used electrolyte material in solid oxide fuel cells (SOFCs). To ensure functionality of an SOFC the electrolyte must be gastight. A prerequisite for gas tightness is sintering of the electrolyte to full density. The densification of zirconia (pure or stabilized) to high percentages (> 98%) of the theoretical density requires sintering temperatures of 1500°C or higher (1,2). Reduced densification temperatures could be realized either by using smaller particle sizes (sub-μm or nanosized powders), by applying an external force, or by the addition of sintering aids. During the sintering of anode-supported planar SOFCs, the external force is provided by the shrinkage of the porous NiO/YSZ cermet substrate. The exploitation of this force reduces the sintering temperature to approx. 1400°C. A subsequent reduction of the sintering temperature to values of ≤ 1300°C can only be realized by the use of well dispersed and packed particle sizes and distributions (including sub-μm and nanosized particles) or the use of sintering additives. Temperatures of ≤ 1300°C are aimed at increasing the possibility of cofiring the electrolyte and the cathode material and thus
reducing the sintering steps during cell manufacturing. To date high temperatures are necessary to densify the electrolyte. Unfortunately, commonly used cathode materials like lanthanum strontium/calcium manganite (LSM/LCM) have a high sinterability at temperatures above 1100°C. This sinterability leads to enhanced densification and grain growth, leading to coarsening of the cathode material and ultimately to a reduction of three-phase boundary points (TPBs). This results in a decrease of cell efficiency. To overcome this problem, two possible variations can be chosen. The first possibility is to enhance cathode materials either by applying novel materials like lanthanum strontium ferrite/cobaltite or by doping LSM/LCM with sintering inhibitors effective at temperatures above 1100°C. The second way is to reduce the densification temperature of the electrolyte by adding sintering aids.

In the literature Al₂O₃ (3, 4), NiO (5), Bi₂O₃ (6), SiO₂ (7-9), TiO₂ (2, 8) and Fe₂O₃ (6, 10) are proposed as sintering aids for zirconia with different stabilizing agents (yttria or calcia, YSZ/CSZ). Silica greatly increases the resistivity of YSZ at low temperatures and titanias (with CSZ), iron and bismuth oxide (both with YSZ) increase resistivity, too. Therefore the use of such additives is ruled out. In contrast, alumina seems to be a good candidate as a sintering additive. Additionally, boron nitride (BN) [11] is identified as a novel sintering aid.

Research Center Jülich, which has been developing and manufacturing planar anode-supported SOFCs for over ten years, deals with the use of sintering aids in two areas. Firstly, in their own planar system (4) and, secondly, together with Siemens in the application of wet chemical coating technologies on the tubular Siemens Westinghouse SOFC design (12). In the planar system, alumina was examined as the sintering aid and in the tubular system BN. This paper deals with the results obtained so far.

**ALUMINA ADDITIONS TO YSZ IN THE PLANAR SYSTEM**

The influence of the addition of 0.77, 2 and 4 wt% alumina to fully yttria-stabilized zirconia with respect to gas tightness and sinterability of the electrolyte layer was investigated using the anode-supported planar SOFCs manufactured at Research Center Jülich. The manufacturing scheme is described in detail elsewhere (4, 13); here only a brief description is presented. After warm pressing and pre-sintering of the substrate composed of NiO and YSZ, an anode, also consisting of NiO and YSZ, and the electrolyte (YSZ) are applied by vacuum slip casting. Both layers were subsequently cofired at 1400°C to electrolyte gas tightness. A cathode functional layer (YSZ and LSM) and a cathode (LSM) are added by wet powder spraying. Finally the cathode bilayer is sintered at 1100°C.

The manufacturing procedure for the investigated electrolyte with the addition of alumina is the same. The only difference is that the YSZ is doped with varying amounts of alumina during pre-processing (suspension preparation). The suspension consists of YSZ, alumina, ethanol and small amounts of dispersant.

**Milling and Calcination of YSZ**

Firstly, examinations were carried out of the effect of milling time on the resulting grain size distribution and the influence of calcination temperature of the YSZ on the helium leak rate of coated substrates. Calcination temperatures were 1100 and 1300°C and...
milling times varied from 24 to 120 hrs. It was found that an increase in calcination temperature leads to larger grain sizes ($d_{50}$) after all milling times. The smallest grain sizes were reached with 1100°C/1200°C pre-calcination temperature after 96 hrs ($d_{50} = 0.17 \mu m$; for comparison: 1300°C and 24 hrs: $d_{50} = 0.39 \mu m$). Subsequently, a matrix of coated samples was developed with all calcination temperatures and three milling times (24, 72 and 120 hrs). The sintering parameters for the electrolyte were: 1400°C with a dwell time of 5 hrs. The lowest obtained leak rates were for samples with 24 hrs milling time and a powder calcination at 1200°C (leak rate: $3 \times 10^{-6}$ mbar l/s cm²; for comparison: sample calcined at 1100°C and a milling time of 120 hrs: $9 \times 10^{-4}$ mbar l/s cm²). Figure 1 shows SEM micrographs of the surfaces (substrate coated with anode functional layer and electrolyte) obtained with different pre-calcination temperatures of the YSZ powder.

Figure 1. SEM micrographs of coated and sintered samples; pre-calcination temperature of YSZ 1100°C (left) and 1200°C (right).

It is obvious that higher calcination temperatures for the YSZ powder lead to more homogeneous and crack-free layers.

Addition of Alumina

The effect of the addition of small amounts of alumina (0.77 to 4 wt%) on the helium leak rate of the electrolyte sintered at 1400°C for 2 or 5 hrs can be seen in figure 2. The best results were yielded by samples with small additions (0.77 wt%) and a dwell time of 5 hrs ($< 1 \times 10^{-7}$ mbar l/s cm²). But even additions of 0.77 and 2 wt% and a reduced dwell time of 2 hrs result in dense electrolyte layers ($< 2 \times 10^{-5}$ mbar l/s cm²). This leak rate is the internal threshold value for electrolytes manufactured by Research Center Jülich.

Effect of Alumina on Cell Performance

After electrolyte coating and sintering selected samples were coated with a cathode functional layer and a cathode layer. These samples (40 x 40 mm²) were then electrochemically characterized at temperatures between 750 and 900°C. Figure 3 shows the comparison of values from samples with alumina additions in the electrolyte and without. It can be seen that alumina additions have a positive effect on cell performance. The current densities at all examined temperatures of samples with alumina additions are slightly higher than of those without.
BORON NITRIDE ADDITIONS TO YSZ IN THE TUBULAR SOFC SYSTEM

Based on the newly released patent (11), tubular SOFCs made by Siemens Westinghouse, Pittsburgh, USA, (including a ceramic interconnect) were coated by wet chemical coating technologies. Special wet powder spraying (WPS), which is an established technology in coating planar SOFCs, was adapted to the tubular cell for the coating of an interlayer and the electrolyte (12). The reason for the application of wet chemical coating technologies is the Siemens Westinghouse's desire to replace the cost-intensive electrolyte coating by electrochemical vapor deposition.

The interlayer composed of LCM and YSZ is added by WPS during rotation of the samples. The interconnect is masked by an adhesive strip to avoid coating it with undesired material. After adding the interlayer and subsequent drying the layer is sintered at temperatures >1000°C. These moderate sintering conditions result in a well-microstructured, porous interlayer.
Electrolyte Deposition

After the pre-sintering of the composite interlayer, the electrolyte (8YSZ) is added by WPS. Different coating parameters like deposition distance, nozzle velocity, spray pressure, various cons and pins, layer thickness, suspension composition etc. were examined. In particular, a statistical process plan for the parameters was developed (14) to enhance the green density of the as-sprayed layer and thus to optimize the gas tightness of the electrolyte. The deposited electrolyte has an overall thickness of 20-30 μm and is composed of two layers. The first one, deposited on the interlayer is additive-free while the top layer is doped with boron nitride. After drying of the layer, various sintering experiments were performed to achieve optimal sintering conditions. It was found that sintering temperatures < 1300°C can be reached. The parameter which characterizes the quality of the layer is the leak rate, as in the planar system. In contrast to the planar system, it was not the helium leak rate that was measured but the permeation of air through the material (pressure increase method). A leak rate of < 2.3 x 10^-4 mbar l/s cm² was termed good and was defined as the threshold value.

Boron Nitride

Various experiments were carried out to define the optimal boron-containing material. Experiments with boric acid (H₃BO₃) led to a high degree of un-reproducibility and in most cases to poor leak rates. This might be explained by the evaporation of the boron oxide before reaction with the electrolyte material. Therefore a housing procedure was created to ensure the non-evaporation of boron. Housing means that the samples were mounted in an alumina cylinder which was closed before sintering. But even this approach yielded poor leak test results. In a next step, the sintering aid boron carrier was changed from boric acid to boron nitride. The reason for the use of boron nitride is that this material is unaffected by the surrounding atmosphere up to temperatures of about 1000°C. As the DTA characterization (see fig. 4) shows, the oxidation of boron nitride begins at temperatures of about 1000°C and reaches a maximum at 1150°C.

![Figure 4. Differential thermal analysis of boron nitride in air (5 K/min)](image_url)

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If samples coated with a boron-nitride-bearing electrolyte were sintered in an alumina housing, only temperatures of < 1300°C were necessary to densify the electrolyte to gas tightness. The amounts of boron nitride in the top layer are in the range of 1-5 wt%. Figure 5 shows a sample a) coated with interlayer; b) coated with electrolyte in the green state; and c) sintered to gas tightness.

The alumina housing can be avoided by using a very small furnace compared to the sample surface. Thus the furnace refractory itself acts as housing.

**Characterization of the Densification Behavior**

A characteristic cross section of a sample with a gastight electrolyte layer is shown in figure 6. The figure shows a 30-μm-thick electrolyte layer on a tubular SOFC without an intermediate interlayer. The grain sizes are in the range of 8-15 μm. The resulting porosity is closed and thus the layer is gas tight. Figure 7 shows part of the same sample at higher magnification. The region between two grains (marked by an arrow) was characterized using SEM-EDX. It was found that at the grain boundary zirconia is depleted while an enrichment of calcium, manganese and lanthanum can be detected. This is a first indication that the densification of the electrolyte layer is supported by a liquid phase. This liquid phase consists mostly of components present in the cathode material. The understanding of the densification behavior of the electrolyte and of the mechanisms yielding this liquid phase are under investigation.

**Figure 5.** Tubular SOFC in different preparation states: interlayer coated and sintered (left), electrolyte coated, green state (middle) and sintered to gastightness (right).
CONCLUSIONS

From the results of alumina additions to YSZ in the planar system, it can be concluded that a pre-calcination temperature for YSZ powder at 1200°C leads to the lowest helium leak rate compared to lower (1100°C) or higher temperatures (1300°C); YSZ powders with a $d_{50}$ in the range of 250-300 nm have the highest sinterability compared to finer grains, enhanced agglomeration tendencies for the smaller grains might be an
explanation; the addition of about 0.77 wt% alumina to the electrolyte either increases the
gas tightness of the layer or reduces the dwell time at sintering temperature; and the cell
performance of samples with additions of alumina in the electrolyte is slightly better than
without.

From the results of electrolyte coatings on tubular SOFCs using different boron carriers
as sintering aids, the use of boric acid leads to un-reproducible results and in most cases
to high leak rates. If boron nitride is used as a sintering aid and the samples are sintered
either in an alumina housing or in small furnaces, gas tightness could be realized at
sintering temperatures < 1300°C. The densification of the electrolyte is supported by a
liquid phase formation with components of the cathode material.

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