PREPARATION OF DOPED CERIA POWDER

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ABSTRACT

The alleged poor sinterability of (doped) ceria was studied for the application as a fuel cell solid electrolyte, and a solution has been proposed. Yttria doped ceria (YDC) powder Ce$_{0.667}$Y$_{0.333}$O$_{1.833}$ was prepared by oxalate coprecipitation through addition of a concentrated yttrium-cerium nitrate solution to a dilute aqueous oxalic acid solution at neutral pH. The precipitate was washed with alcohol and calcined at 700°C. Coprecipitation conditions were critical for the quality of the resulting oxide powder, of which the average particle size was a key parameter. Compacted into pellets, relative densities attained >95% and > 98% of theoretical after firing for 4 hours at 1300°C and 1500°C respectively. Sample "embedding" with YDC powder further improved the final density. Standard conductivity behaviour of the samples was observed. The powder could equally be tape cast and sintered to dense films.

INTRODUCTION

In recent years, doped ceria (DC) has become attractive as an alternative solid electrolyte to yttria-stabilized zirconia (YSZ) for the application in solid oxide fuel cells, SOFC (1,2). Because of its higher ionic conductivity, the fuel cell operating temperature may be lowered from currently 1000°C down to 800°C, while retaining a comparable power output. This bears several advantages such as improved thermodynamic efficiency and lifetime, and the possible use of cheaper cell stack and housing components. Two of the major problems, absent in the case of YSZ, with the ceria material are 1) its ill-sinterability and 2) its reducibility (3).

The latter of the two problems leads to a substantial electronic conductivity of the ceria in a fuel cell environment, thereby partly shorting the cell which results in a power loss. This problem can be addressed by protecting a ceria support electrolyte with a thin layer of dense YSZ (4,5). For mechanical stability, a trilayer structure DC-YSZ-DC
could also be envisaged. This topic is one of the future interests of this laboratory, emphasizing tape casting as the standard fabrication technique.

The former of the aforementioned problems was the topic of this study. Ceria is renowned to be difficult to densify. Densities of 95% and lower of theoretical are usually reported (5-10), and typically high sintering temperatures of 1550 to 1800°C were employed. High density is desirable for good electrical and mechanical properties.

In this work, yttria doped ceria powder was produced, its characteristics and sintering behaviour as compacted pellets studied, and finally applied to the fabrication of dense films by the tape cast technique.

**EXPERIMENTAL**

Coprecipitation of the metal nitrates with oxalic acid was used to produce an intimately mixed oxalate precursor, which was then decomposed to the oxide. The coprecipitation procedure is established in the literature (7, 11-14) as a superior way of producing well-sinterable powders, because of the resulting fine particle size, absence of large hard agglomerates, and homogeneity of the dopant and matrix oxide mixture. Yttrium was chosen as the dopant because of its price and, in view of the future application, its chemical compatibility with YSZ, which contains the same dopant ion. A high dopant content of 33 mol% YO1.5 was initially selected, based upon the argument that the formation of an extended solid solution may suppress CeO2 evaporation at high temperatures. YDC retains the fluorite phase up to >40 mol% YO1.5 (15); the ratio 2:1 for Ce:Y was chosen for convenience.

The starting materials used were Ce(NO3)3.6H2O (>98%), Y(NO3)3.6H2O (99.9%), and H2C2O4.2H2O (>99.5%). Proper amounts of the nitrate salts were weighed, dissolved in dist. H2O and then added from a buret to a stirred oxalic acid solution (reverse strike). The concentrations of the mixed nitrates solution and of the oxalic acid solution were varied. The pH of the oxalic acid solution was varied and for each variation maintained throughout the precipitation reaction, by the addition of dilute ammonium hydroxide NH4OH. The precipitate was vacuum-filtered and washed with H2O (5x) to remove oxalate and nitrate anions, and finally with pure ethanol EtOH (5x) to dewater. After drying overnight at 50°C, the oxalate precursor was decomposed to the oxide at 700°C for 1 hr. The oxide yield was always over 99%. The resulting powder was compacted into pellets of ~20 mm in diameter and 1-2 mm thick, uniaxially pressed at 200 MPa and fired at 1500°C for 4 h (heating and cooling rates 150°C/h). Densities were measured by the Archimedes method using H2O, and expressed as values relative to the theoretical density of Ce0.667Y0.333O1.833 (33YDC). The value of the latter was calculated from the empirical lattice parameter equation for YDC in (16).

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The powders were characterized by thermogravimetric analysis-differential thermal analysis TG-DTA of the oxalates, and particle size distribution measurements (PSD) and X-ray diffractometry of the oxides. Often a powder batch was ballmilled to reduce the particle agglomerates size. Wet ballmilling (in isopropanol) was done with zirconia balls in zirconia jars. All the fired samples were examined by scanning electron microscopy SEM, equipped with an EDAX facility. The conductivity of sintered samples was determined in air between 300 and 1000°C by impedance spectroscopy (Pt paste electrodes).

RESULTS

TG-DTA

A typical TG-DTA curve of the oxalate precursor is shown in Fig. 1. As noted before in the literature in the case of coprecipitation (14,17,18), no separate yttrium and cerous oxalate "peaks" were observed. Yttrium oxalate alone decomposes via the carbonate to the oxide only above 750-800°C (19,20). This indicates that already the oxalate constitutes a solid solution, \((\text{CeO}_{6.67}\text{Y}_{0.333})_2\text{(C}_2\text{O}_4)_3\cdot10\text{H}_2\text{O}\), which decomposes to the oxide at a temperature close to but always lower than the value for pure cerous oxalate, 370-400°C (20,21). From the above chemical formula, theoretical weight losses upon dehydration at 120°C and decomposition at 340°C are calculated to -26.1% and -55.8% respectively, in good agreement with the experiment.

In the case of a mixture of cerous oxalate and yttrium oxalate, deliberately produced by a direct strike precipitation (addition of the oxalic acid solution to the nitrate mixture), a very large exothermic decomposition peak at around 400°C was observed. This behaviour corresponds to that of separate cerous oxalate (21). The resulting powder was yellow (the colour of CeO₂ alone) rather than ivory as in the case of a properly doped powder. A powder with this characteristic (yellowish, large exothermic peak in the TG-DTA fingerprint) was generally ill-compactible and poorly sinterable, due to larger particle sizes and the lack of a homogeneous distribution of the dopant.

From Fig. 1, crystallisation of the oxide solid solution could be obtained at as low as 400°C for long calcination times. However, for calcination temperatures of up to 600°C with a fixed hold time of only 1 hour at the maximum temperature, decomposition was not yet complete for the whole powder batch. On the other hand, powders calcined at 750°C and higher were increasingly difficult to compact, the pellets often breaking apart. As a good compromise, the calcination temperature was therefore fixed at 700°C for all experiments.
Coprecipitation Parameters

Effect of oxalic acid concentration. The oxalic acid solution was varied between 0.4 M down to 0.0225 M, for a constant nitrates solution of 1 M and a \( \text{pH} \) between 6.7 and 6.9. The resulting average particle sizes as obtained from the PSD measurements, as well as the obtained density of the samples, pressed at 200 MPa and fired in air at 1500°C for 4 h, are plotted in Fig. 2a. A clear correlation between the oxalic acid solution concentration, the oxide powder particle size (calcination 700°C/1 h) and the resulting relative density is demonstrated, the best results occurring for \( \leq 0.06 \) M oxalic acid solution. With a too concentrated oxalic acid solution, separate cerous and yttrium oxalates are precipitated as was indicated by the yellow colour of the resulting oxide mixture and a large decomposition peak at around 390°C in the TG-DTA fingerprint.

Effect of nitrates concentration. To a constant dilute oxalic acid solution of 0.06 M, at a \( \text{pH} \) of 6.7-6.9, nitrate solutions with concentrations varying between 3 M and 0.05 M were added. The average particle size of the resulting oxide powder, as well as the fired density of compacted samples, is plotted in Fig. 2b. Again a correlation between the nitrates concentration, oxide powder particle size and relative density after firing is demonstrated. Though the effect is less pronounced as with the oxalic acid concentration variation (Fig. 2a), it is nevertheless important to keep the nitrates concentration at \( >1 \) M.

Effect of pH. For a series of 1 M nitrate solutions added to 0.05 M oxalic acid solutions, the \( \text{pH} \) was varied from neutral down to the "natural \( \text{pH} \)" of the mixture (i.e. without any NH\(_4\)OH addition). The latter lay at \( \text{pH} \approx 2.0 \) for the 0.05 M oxalic acid solution, further dropping to a final \( \text{pH} \) of \(-1.7 \) upon slow addition of the acidic nitrate solution. For the other cases (\( \text{pH} \) 3.0, 4.0, 5.0, 6.9), the \( \text{pH} \) was kept approximately constant through NH\(_4\)OH addition during the precipitation reaction. A similar plot as for Fig. 2a,b is shown for the effect of \( \text{pH} \) in Fig. 2c. Whereas no influence of \( \text{pH} \) is apparent in the \( \text{pH} \) range 3-7, the powder obtained from the precipitation conducted at "natural \( \text{pH} \)" was clearly inferior. Again a large decomposition peak at around 390°C in the TG-DTA fingerprint, as observed for this case, and the yellow powder colour were indicative of bad mixing in the precursor already.

Sintering Parameters

Effect of sample "embedding". Embedding of pellets in coarse powder of the same composition was examined in order to prevent loss of CeO\(_2\) at their surfaces. Whereas the freely exposed surface ("top side" of the pellet) usually sintered dense, the "bottom side" in contact with the substrate plate (Al\(_2\)O\(_3\)) often showed a 2-3 \( \mu \)m deep porous layer. As verified by EDAX, this layer was significantly richer in yttrium than the bulk of the sample. In Fig. 3, the surfaces and fracture views of 2 samples (of a standard
batch) are shown, one of which was sintered entirely embedded with coarse YDC powder whereas the other wasn't. Final densities were 99.2 and 98.5% of theoretical respectively. The embedded sample (99.2%) was differently colored (beige brown rather than yellow sandy) and translucent. Most striking of all is the difference in grain size between both pellets, though they were fired at the same temperature (1500°C/4 h).

Alternatively, surface evaporation of a pellet was suppressed by ballmilling the powder prior to compaction. This introduces, however, an extra process step and a possible contamination. In general, even poor powders of large average particle size could be sintered to acceptable densities after ballmilling and compacting, as summarized in Fig. 4. It displays an overview of resulting pellet densities with respect to the average particle size of the starting powders. Both milled and "as calcined" powders are indicated. Clearly the powder must be submicron in order to achieve ~98% density.

Effect of sintering temperature. In Fig. 5, the final densities of samples from a standard batch are displayed as a function of the maximum firing temperature (non-embedded samples). After firing at 1200 °C, though already 93% dense, the pellet was still an agglomerate of small particles, virtually unchanged from the starting powder. After firing at 1300°C and higher, pore elimination and hence densification had markedly increased, as observed from SEM. The values in Fig. 5 are among the best reported so far. For comparison, values are also plotted from a very recent work (14), where Gd-DC was prepared in a similar way as employed here (oxalate coprecipitation, 200 MPa compacts, hold time at maximum temperature 4 hrs). Others (22) using a similar procedure obtained 95% density after firing at 1600°C for 2 h. 1300°C was in our case the necessary but sufficient lower temperature limit at which doped ceria can be densified. This was reconfirmed by merely increasing the residence time at the plateau of 1300°C to 48 h, resulting in a 98.8% density of theoretical.

Conductivity

The conductivity in air of 33 YDC pellets (>98% dense) was measured between 300 and 1000°C and represented in an Arrhenius graph in Fig. 6. It compares well with other reported values (4,6,10) for YDC of a similar composition. It is expected that at the composition of maximum conductivity, around 15-20 mol% YO$_{1.5}$ (22,23), the values will increase by a multiple factor.

Tape Casting

A large batch of 33 YDC was prepared by the established formulation : 1 M nitrate, 0.05 M oxalic acid, neutral pH, ethanol-washed precipitate, and calcination at 700°C for 1 h. The powder was ballmilled in isopropanol down to below 0.5 μm average
particle diameter. A tape cast slurry composition was used identical as for 8YSZ, as previously established in this laboratory (24). After slurry milling, casting and drying, discs of 30-60 mm in diameter were punched from the tape for sintering. The discs were put on a bed of coarse YDC powder and entirely covered -"embedded"- with the same to a load of about 0.5 g/cm², and fired according to the following schedule: room temperature to 600°C at 30°C/h, 600°C to 1000°C at 100°C/h, 1000°C to 1670°C at 220°C/h, residence time at 1670°C being 2 h, cooldown at 400°C/h. The slow rate at low temperature allows a gentle burnout of the organic part of the tape, whereas the fast rates at high temperature improve the densification. The maximum temperature plateau had to be increased from 1500°C to 1670°C to obtain dense samples. The resulting thin films (100 µm) were beige transparent, >96% dense, and reasonably flat. This outcome is expected to improve (i.e higher final density and/or lower sintering temperature) by further optimising the parameters relating to the tape cast procedure such as the BET surface area of the powder, the slurry viscosity upon casting and the binder amount in the slurry. The green density of the tape, 37% for the above case, still needs to be improved to >40%.

FURTHER WORK

In a next step, the tape casting procedure has to be optimised as just discussed. The dopant content and nature can be varied to test the general validity of the proposed precipitation procedure. In a preliminary trial, powders of 10, 15, 20 and 25 mol% YDC were prepared, employing the standard procedure outlined above. Each powder could be fired 99.0% dense (1500°C/4 h). Tapes with the composition corresponding to the conductivity maximum will then be fabricated. No problems are anticipated when using other dopant ions, except for a change in the maximum sintering temperature.

CONCLUSION

Yttria-doped ceria powder was successfully prepared by oxalate coprecipitation. The conditions of the precipitation bath, especially the concentrations of the reagents involved, proved critical for the quality of the resulting oxide powder, which has to be intimately mixed and of submicron particle size. Optimal conditions were established as ≈1 M of metal nitrates solution, ≲0.05 M of neutral oxalic acid solution, ethanol-washing of the precipitate and calcination at 700°C. Compacts of the powder could be fired to near 99% density at 1500°C (4 h) and >95% at as low a temperature as 1300°C (4 h). Embedding of samples with YDC powder improved the final density. The samples showed good conductivity behaviour. The powder could be tape cast and sintered to dense films.
ACKNOWLEDGEMENT

This work was conducted under the financial support of the Science and Technology Agency, Japan, which is herewith most gratefully acknowledged.

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Fig. 1 TG-DTA curve of the oxalate precursor (10mg) \( \text{Ce}_{0.667}\text{Y}_{0.333}\text{O}_3\cdot\text{H}_2\text{O} \). Heating rate 5°C/min.

Fig. 2 Average particle size of oxide powder (open circles) and obtained density of sintered compacts (1500°C/4 h, closed circles) as a function of coprecipitation bath parameters.
Fig. 3  SEM micrographs of sintered 33YDC samples (1500°C/4 h). The left and right columns correspond to a sample which was fired "freely" in air (left) and em-bedded in coarse YDC powder (right), respectively. The top row represents the top surfaces of the pellets, the middle row the bottom surfaces, and the bottom row fracture views. The lower left graph was taken on the bottom edge to illustrate the CeO₂ evaporation, resulting in a few μm deep porous layer. Towards the bulk, both samples are equally dense (as shown on the lower right hand side).
samples pressed at 200 MPa and fired at 1500°C / 4 h

Fig. 4 Overview of obtained densities of compacts as a function of the average particle size of the starting powder.

Fig. 5 Fired density of powder compacts of a standard batch, compared with the recent literature (200 MPa, residence time 4 h at the maximum temperature).

Fig. 6 Arrhenius plot for the samples conductivity (in air), compared with other values for similarly doped YDC.
