THIN ANODE SUPPORTED SOFC

S. Primdahl, M. J. Jørgensen, C. Bagger and B. Kindl
Riso National Laboratory, Materials Research Dept., DK-4000, Roskilde, Denmark

ABSTRACT

Some of the most important parameters for preparing anode supported electrolytes for solid oxide fuel cells (SOFC) by co-sintering are discussed. Reported procedures for fabrication of YSZ electrolytes on NiO/YSZ anode precursor structures are listed, and a recent approach taken at Riso National Laboratory is presented. By cheap, scaleable processes a 10 to 25 μm thick electrolyte is co-sintered on a NiO/YSZ support only 200 to 250 μm thick. The produced half-cells are flexible and exhibit a tensile strength exceeding 150 MPa. After deposition of a composite cathode the cells attained a performance of about 0.4 Ωcm² at 850°C in hydrogen with 2% water against air. Additional experiments indicate that performance is predominantly limited by diffusion impedance in the support and by cathode performance. Remedies for improvement of performance are thus available.

INTRODUCTION

Using an SOFC operation temperature in the range of 700 to 850°C instead of 1000°C, a wider range of materials can be used, especially metal alloys for the cell interconnect (1). Due to thermal activation of electrode processes and electrolyte conductivity, the lower temperature calls for highly efficient electrodes and an electrolyte with high performance. One way to increase the electrolyte performance is to reduce the thickness.

The choice of materials for the supporting component has a number of important consequences, relating primarily to i) reactivity with the electrolyte, ii) cell strength, iii) gas diffusion limitations, iv) sintering compatibility, and v) cost.

i) A thin yttria-stabilized zirconia (YSZ) electrolyte supported on a Ni/YSZ anode has been demonstrated (2-4). The limited reactivity (5) between these materials allows for co-sintering at temperatures up to 1500°C without loss of anode performance (6), making component production by cheap wet-ceramic processes feasible. Calendering of laminated tapecast foils is a possible technique (4) as well as sequential tape casting, i.e. casting one layer on top of another (3).

ii) Electrolyte supported cells are frequently based on a 100 to 200 μm thick dense YSZ electrolyte in order to obtain sufficient strength for handling and mounting of cells (7). For a porous structure to have the same strength, a higher thickness or a stronger material is normally required.
iii) The support must be thin and porous enough to allow gas access to the electrodes without significant diffusion limitation. This requirement is easier to fulfill on the anode side for H\textsubscript{2}/H\textsubscript{2}O than for O\textsubscript{2}/N\textsubscript{2} on the cathode side, due to the considerably lower binary diffusion coefficient of the latter (8,9). The electrocatalytically effective thickness of Ni/YSZ cermet anodes has been shown to be about 10 \textmu m at 1000°C (10,11), and Ni/YSZ based cermets with a conductivity in the order of $10^2$-$10^3$ S/cm have been demonstrated (12,13). Thus, to ensure optimum anode performance and adequate current collection the structure need not be more than about 50 \textmu m thick, provided the spacing between points of contact are about 1 mm or less.

iv) Both sintering contraction and the thermal expansion coefficient (TEC) of the support material and the electrolyte must be fairly well matched. Differences in sintering contraction can lead to bending and warping during sintering (14). Differences in TEC may cause micro-cracking of the layer experiencing tensile stress, whereby delamination in the interface or crack propagation to the other component can occur (6,15).

v) Cost of the support material is an important issue, depending on materials selection, purity and component volume (thickness). Cost-effective alternatives to YSZ in the anode support such as TiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} have been investigated (16). Another interesting detail is the reported use of YSZ with 8 mol\% Y\textsubscript{2}O\textsubscript{3} (8YSZ) in the anode support structure (2,3). As oxide ion conductivity is not required in this component, cheaper 3YSZ could be used, with the further benefit of higher material strength due to the tetragonal-monoclinic transformation toughening (17).

In addition to these considerations for the support, the thickness of the electrolyte is a topic for discussion. Generally a thickness well below 50 \textmu m is required at 700 to 850°C to avoid the electrolyte being the major limitation to cell performance. Dense YSZ layers well below 10 \textmu m have been reported (3). Current constriction effects are known to add significantly to the electrolyte resistance when the electrolyte thickness approaches the distance between adjacent electrode particles (18). Furthermore, the solubility of Mn from the cathode in the electrolyte has been demonstrated to increase the electronic conductivity in the electrolyte (19). For these reasons an electrolyte thickness in the interval of 10 to 25 \textmu m is suggested to be the most promising compromise. Dimensions of anode-material supported SOFC produced by co-sintering are given in Table I.

Table I Reported processes for anode supported cells.

| Developer       | Process                                      | Support thickness | Electrolyte thickness |
|-----------------|----------------------------------------------|-------------------|-----------------------|
| Jülich (2)      | powder processing and pressing of AS, partial sintering, vacuum impregnation A+E, co-sintering | 1.7 mm           | 15 \textmu m          |
| Allied Signal (4) | lamination of tapecast, co-sintering         | 500-750 \textmu m | 2 \textmu m          |
| EPFL (3)        | seq. tape casting, co-sintering              | 200 \textmu m     | 6-10 \textmu m       |
| Risø            | seq. tape casting, co-sintering              | 200-300 \textmu m | 10-25 \textmu m      |

AS: anode support, A: anode, E: electrolyte
In summary, a number of important criteria appear to be adequately fulfilled by choosing the NiO/YSZ composite anode precursor structure as a support for a thin electrolyte fabricated by co-sintering. Inspection of reported methods indicate a further potential for exploiting the economic advantages of scaleable, wet-ceramic processes.

Present Approach

In the following a recent approach (20) taken at Risø National Laboratory towards fabrication of low-cost anode-supported planar half-cells is presented together with key characteristics of the product. The half-cells comprise a 10 to 25 μm thick dense YSZ electrolyte on a 200 to 300 μm thick, porous NiO/YSZ based support. A functional NiO/YSZ anode layer of about 15 μm is established between these layers.

The following alternate production sequences are used to fabricate the supported electrolyte.

A) Tape casting of an 8YSZ electrolyte slip on a carrier film, followed by spray-painting of the NiO/8YSZ anode slurry and finally tape casting of a NiO/3YSZ based slip to form the supporting structure.

B) Tape casting of a NiO/3YSZ based slip to form the supporting structure on a carrier film, followed by spray painting of the NiO/8YSZ anode slurry and spray painting of an 8YSZ electrolyte slurry.

Finally the half-cells are punched and sintered, and an LSM/YSZ composite cathode is deposited by spray painting and sintered.

The described production lines represent a combination of some of the most simple and cheap processes known for production of SOFC components. Furthermore, the processes are scaleable and can be incorporated in a production line with a minimum of handling steps.

EXPERIMENTAL

Co-sintering of two materials may require some adjustment of the sintering behavior to obtain flat and flawless samples. In this case an existing 8YSZ electrolyte material was accepted without modifications to ensure the achievement of a dense electrolyte layer with high conductivity. For the support structure the total sintering shrinkage and porosity was varied by application of different types of NiO and YSZ with different powder morphology, and by addition of pore formers such as corn starch. The effect of small amounts of MnO₂ as a sintering control agent has been investigated (20).

The variations in sintering behavior were illustrated by dilatometry on rolled cylinders of tapecast electrolyte tape with and without 1 metal-atom% (a/o) Mn and for NiO/3YSZ-based support tapes with and without 3.5 a/o Mn.
Supported electrolytes of 1x9 cm² were produced according to procedure B) without addition of pore formers. After sintering at 1300°C/12h the fracture strength was measured by uniaxial tension according to specifications given elsewhere (21). These values were taken to represent the strength of cells. Deposition of LSM/YSZ cathodes at 1100°C was assumed not to lower the overall strength.

Symmetrical test cells comprising two identical anodes and supports on opposing sides of an electrolyte were produced for electrochemical tests. Samples with and without 40 solids-v/o corn starch in the support were produced from green substrates produced by method A) above and removed from the carrier film. Identical anode and support structures were applied on the electrolyte side by spray painting of the NiO/8YSZ anode slurry and tape casting of the NiO/3YSZ based slip. Test cells of 5x5 mm² were cut and sintered at 1300°C/12h. The cell edges were ground to avoid short circuits. The symmetrical cells were characterized in a two-electrode four-wire arrangement by impedance spectroscopy at 850°C in hydrogen with 3% water. Diffusion impedance and electrode impedance could be discriminated by the time constants (22).

Sintered supported electrolytes of 5x5 cm² produced by method A) and B) above were provided with a (La_{0.15}Sr_{0.85})_{0.90}MnO_{3±δ} (LSM15)/YSZ composite cathode of 5 to 10 μm sintered at 1100°C/2h, and a tapecast LSM15-foil of 50 μm sintered at 1100°C for current collection. Cell test was conducted at 750 to 950°C in 300 l/h hydrogen with 2% water vs. 100 l/h air in a setup described elsewhere (23). Pt-meshes of 5.7 to 7 cm² were applied on both sides for adequate current collection and gas access.

RESULTS AND DISCUSSION

Sintering Contraction

Sintering curves for electrolytes and support structures established by dilatometry are given in Figure 1. A significant difference in sintering contraction with temperature and total sintering contraction is observed for the 8YSZ electrolyte and the NiO/3YSZ support structure. By addition of MnO₂ as a sintering control agent, the total sintering contraction of the two components is considerably better matched. Flawless half-cells comprising electrolyte and support sintered according to the curves 2) and 3) have been fabricated. Apparently substantial differences in sintering contraction could be tolerated during sintering, but a fairly accurate match of total contraction is required to obtain flat samples without bending and warping at the edges. The total contraction was adjusted by modifications in the support slip recipe and by selection of sintering temperature and time.

Sample Appearance

A large number of supported electrolytes have been produced by method A) and B). So far, sizes were 5x5 cm², 12x12 cm² and 12 cm in diameter. The losses during fabrication and sintering were very low. Sintered cells appeared smooth and flawless.

796       Electrochemical Society Proceedings Volume 99-19
The cell microstructure as observed on fracture surfaces by low vacuum scanning electron microscopy (LV-SEM) is given in Figure 2. Total dimensions are indicated in Figure 2A, where a full cell including cathode and cathode current collector is shown after reduction of the anode and cell test. There is no pore former in the support. The effect on support microstructure of adding 40 solids v/o corn starch as a pore former is seen in Figure 2B.

**Strength**

The tensile fracture strength of 30 unreduced half-cells tested at room temperature is given in a Weibull plot, Figure 3. The observed fracture strength of about 150 MPa is considered a minimum value, as all samples broke at the edge of the mounting tabs. The obtained strength is comparable to the strength of dense 8YSZ tapecast electrolyte foils, (21). Addition of a pore former will probably decrease the strength of the cells somewhat, and a delicate balance between strength, thickness and porosity must be maintained for optimum performance. Furthermore, the cells are remarkably flexible, tolerating substantial deformation by bending. This is thought to be a consequence of the combination of the thin structure and the use of 3YSZ in the support structure exhibiting transformation toughening (17).

**Symmetrical Cells**

Symmetrical cells produced with and without 40 solids-v/o corn starch for pore formation in the support structure are tested in hydrogen with 3% water at 850°C. Impedance spectra are given in Figure 4 after normalization to electrode area and subtraction of the series resistance. In both spectra two well-separated arcs are observed with approximate summit frequencies of 1 to 10 kHz and 10 to 50 Hz. From studies on electrolyte supported cells with 50 μm thick Ni/YSZ cermet anodes, the electrode response is recognized to be the arc with a characteristic frequency in the range of 1 to 10 kHz (22). A resistive value of about 60 to 90 mΩcm² is comparable to some of the best results obtained on Ni/YSZ based cermet anodes (24). The impedance arc at 10 to 50 Hz is recognized to be gas diffusion impedance (22). Diffusion outside the anode structure is known to amount to no more than 30 mΩcm² under the given conditions in this setup (22). Subtracting the electrode impedance and the expected gas diffusion impedance outside the porous structure, it is observed how the remaining impedance, assumed to be diffusion impedance in the porous support, is reduced from about 150 mΩcm² to about 80 mΩcm² by addition of the pore former. The electrolyte resistance observed at 850°C is about 70 and 40 mΩcm² for the two samples, respectively. The thickness of these electrolytes is about 15 μm, yielding a calculated electrolyte resistance of about 20 mΩcm², based on a conductivity of 0.18 S/cm at 1000°C for dense 8YSZ (25), and an activation energy of 0.8 eV. The discrepancy is assumed to arise in current constriction in the electrolyte and contamination of the electrolyte material by migration of Ni and Mn into the structure during sintering. The support structure is not expected to contribute a significant ohmic resistance, as an in-plane conductivity well above 100 S/cm is measured at 850°C.
**Cell Tests**

Two i-V curves obtained on two anode supported cells at 860°C and 890°C, respectively, are presented in Figure 5. The two cells are produced with different NiO powders and by methods A) and B), respectively. OCV values in agreement with theory indicate that the 15 μm thick electrolyte is dense without pinholes. The obtained area-specific resistances are 0.40 and 0.42 Ωcm² based on the overall slope of the measured curves. A value of 0.8 Ωcm² at 750°C indicates an apparent activation energy of about 0.6 eV. No pore former has been added to the supports. Based on the results presented for the symmetrical cells, an improvement in the presented cell performance is expected to be obtainable in this way. Furthermore, the cathode is indicated to be a major contributor to the cell resistance, based on the data given above for the electrolyte and the anode.

**SUMMARY**

A cheap, scaleable method for producing thin, strong, flexible and efficient anode supported cells with low production losses is developed. NiO/3YSZ supports are about 200 to 250 μm thick, 8YSZ electrolytes are 10 to 25 μm thick. The strength and flexibility is primarily ascribed to the use of TZ3Y in the support structure, and the low cell thickness. Cell performance of 420 mΩcm² at 860°C in hydrogen with 2% water vs. air is demonstrated. The anode polarization resistance and the electrolyte series resistance are demonstrated to amount to about 130 mΩcm² under similar conditions. The major contributors to the cell impedance are diffusion in the Ni/YSZ support of about 120 mΩcm², and cathode impedance. The diffusion impedance is demonstrated to decrease by addition of a pore former to the support structure, and the cathodes applied for cell testing can readily be replaced with better cathodes. Cell improvements are therefore expected to be achieved in the future.

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Figure 1  Dilatometry curves obtained on rolled cylinders of tape-cast YSZ electrolyte and NiO/YSZ support films produced separately. 1) NiO/3YSZ support structure, 2) NiO/3YSZ support structure with 3.5 a/o MnO, and 3) 8YSZ electrolyte.

Figure 2A  LV-SEM micrograph showing a fracture surface of a full cell comprising a reduced support (without pore former) and an LSM15/YSZ cathode. A: anode, E: electrolyte, C: cathode.
Figure 2B  LV-SEM micrograph showing a fracture surface of an as sintered half-cell fabricated with 40 solids v/o corn starch as pore former. A: anode, E: electrolyte.

Figure 3  Weibull plot giving the tensile fracture strength of the support/anode/electrolyte structure after sintering at 1300°C/12h. Measured in uniaxial tension (21) at ambient temperature.
Figure 4  Impedance spectra for two symmetrical cells (see insert) in hydrogen with 3% water at 850°C after normalization to electrode area. Squares: no pore former, circles: 40 solids v/o corn starch as a pore former.

Figure 5  i-V-curves for two 5×5 cm² cells with different NiO powders no pore former in the supports.