ANODE SUPPORTED THIN ZIRCONIA BASED CELLS FOR INTERMEDIATE TEMPERATURE SOFC

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ABSTRACT

Ni-YSZ anode supports show a fundamentally different microstructure from screenprinted Ni-YSZ anodes on YSZ electrolyte supports. Of high density and composed of fine zirconia and nickel oxide to allow for cofiring with a thin zirconia electrolyte film (5 μm), the anode support shows advantages of adequate strength and increased electrochemical activity probably not only limited to the TPB, unlike screenprinted porous anodes. Areas up to 100 cm² have been fabricated. Electrochemical cell testing produced results of >80% fuel utilisation, 35% electrical efficiency and >20 W at 800°C using hydrogen fuel. Unusually high ohmic loss (> 3 x theoretical) on supported cells is consistently observed. The smallest loss is measured when employing thin dense cathodes of a mixed conducting material. Overall cell performance (at ≤ 800°C) is more determined by the cathode than by the anode support.

INTRODUCTION

Ever since the pioneering work by Allied Signal (1) and LBL (2), that demonstrated high power density using thin zirconia electrolytes on an anode support, SOFC research has intensified this approach. The main advantage, compared to an electrolyte support concept, lies in a reduction of operating temperature from > 900°C to < 800°C, for at least equal power density. This improves durability and cost effectiveness of the whole system, since degradation phenomena are decelerated and because inexpensive, thermomechanically compatible iron-chromium interconnecting sheets can be used. Cofiring of anode and electrolyte saves a thermal cycle. Fabrication of the structure can be achieved with established and affordable ceramic procedures for mass production. In the cited work (1,2), calendering and dip coating were used for processing. Our development has from the beginning focussed on aqueous tape casting (3).

The anode supports are made from fine starting powders, in order to allow for sufficient shrinkage and densification of the cofired thin electrolyte film. They hereby offer resulting microstructural properties that show, with respect to ordinary anodes screenprinted on YSZ electrolyte supports, advantages of adequate strength and better electrochemical activity probably not only limited to the triple phase boundary (TPB). The present document summarizes our cell development status (i.e. including cathode studies) based upon anode supports, which could be upscaled to 100 cm².

EXPERIMENTAL

Powders used for fabricating anode supports are commercial 8YSZ (Tosoh) and NiO prepared in house through pyrolysis of precursor salts (acetate, carbonate). A 50-50 wt% powder mix NiO-8YSZ is dispersed in water with polyelectrolyte and a binder
system, for example polyvinylalcohol/glycerol. A same slurry formulation is prepared for the 8YSZ electrolyte alone. Both slurries are co-cast on glass substrates, using an in-house designed doctor blade device. Occasionally, a ceria-yttria (15CYO) electrolyte layer was co-cast on top of the zirconia film (4). More recently, such layers were produced by postfiring cast CYO films at lower sintering temperature (1200°C) (5).

Samples are punched from the dried tapes and co-fired at 1350°C. Single step firing between porous zirconia boards has been achieved. Small discs of 10 cm², for screen testing of cathodes, to regular size plates of 100 cm² have been produced. Reproducible thicknesses amount to 0.15-0.2 mm for the support and 5-8 µm for the electrolyte. For performance comparison, regular cermets for screenprinting on electrolyte supports have been prepared and tested. These consist of commercial coarse zirconia (8YSZ or ZrO₂ from Magnesium Elektron, UK, 20 µm avg. size), drymilled to a broad particle size distribution of 0.2-15 µm (avg. 5 µm, 1 m²/g), mixed in a 44-56 wt% ratio with in-house prepared NiO (calcined at 900°C, 0.5 µm, 2 m²/g).

LaSrMnO₃ and LaSrCoO₃ cathode powders, unless mentioned otherwise, were prepared using the citrate gel route (6). Calcination at 700-900°C for 2 h yields sinteractive powders of XRD-pure cubic perovskite phase. Screen printable inks were made on a triple roll alumina mill, using terpineol-ethylcellulose as a vehicle. Inks were printed layer for layer through stainless steel mesh (250 or 325). Weight deposits of the cathodes typically amount to 20 mg/cm²² for thicknesses of 40 µm and an overall porosity of 50% after firing. Sintering temperature was varied between 1100 and 1200°C. The cathode areas were limited to 1 cm², except for the larger plates (100 cm²). Several compositions and combinations have been screen tested. Stoichiometric LSM (La₀.₈₄Sr₀.₁₆MnO₃) from Missouri-Rolla, sintered at 1100°C, was used as baseline reference. Substoichiometric LSM was mixed and printed with fine 8YSZ (Tosoh) in a 50-50 wt% proportion and fired to 1200°C. A higher sintering temperature was required here to promote adhesion of the composite to the electrolyte. Substoichiometric LSM was chosen for this case, to avoid solid state reaction between the perovskite and zirconia at the higher sintering temperature. Alternatively, we also tested gradient cathodes based on LSM-YSZ/LSM-LSC composites made available through a European collaboration programme (7).

La₀.₆Sr₀.₄Co₀.₂Fe₀.₈O₃ (LSCF, Praxair) or La₀.₅Sr₀.₅CoO₃ (LSC), when tested on thin zirconia at ≤ 750°C, was used as an unfired cathode (in situ) for short test duration (<200 h), to avoid excessive interfacial reaction. In presence of a ceria electrolyte coating on the zirconia film, the LSCF cathode was fired (1100°C/2h) as a 60-40 wt% composite with 15CYO (4). Finally, also dense sputtered LSC (8) was applied as submicron layer (0.2 µm) directly on 8YSZ electrolyte.

Too small Ni particles at the outer anode support surface will prevent proper current collection. Therefore an additional layer was deposited on this anode face, consisting of either a 10 µm silver paint layer (for test durations <200 h) or of a nickel-enriched cermet layer (90/10), which was co-fired with the support. Ni-felt was glued to the support with anode paste and Pt-mesh to the cathode with LSCF or LSC paste. Cells were mounted seallessly between Inconel 600 flanges using ceramic fiber cushions, under an external springload. Excess fuel (H₂, 3% H₂O), except for the 100 cm² samples, was flushed to the anode, and excess air to the cathode. Four lead i-V characteristics were recorded with potentiostats (10 A Wenking HP 88 or in house built 50 A galvanostat) and diagnostics performed by impedance spectroscopy (Zahner Elektrik IM6). This also allowed to separate ohmic from polarisation losses.
RESULTS

Screenprinted Anode

Unlike anode supports, screenprinted anodes are very porous (40-50%) and contain both small and large YSZ grains (9). The large grains fix a structural frame through which smaller nickel particles can percolate, the small grains improve adhesion to the electrolyte and reduce nickel sintering by preventing excessive coagulation. The grain size mixture was here achieved from a single batch through milling of coarse commercial zirconia, both insulating monoclinic ZrO$_2$ and ionically conducting 8YSZ. Electrochemical anode performance is reported to be governed by the TPB length (10). It is shown for the two anode combinations in Fig. 1. Since the same result is obtained regardless of the ionic conductivity in the cermet, only Ni at interfacial TPB is believed to be active. Anodic loss amounts to roughly 0.16 V at 1 A/cm$^2$ and 800°C, which corresponds to a cermet performance elsewhere reported for operation at 1000°C (11).

Anode Support

As mentioned, the produced nickel oxide grain size is similar to that of the zirconia starting powder. This, among others, allows to cofire and densify the electrolyte, which consists of zirconia particles of the same starting powder. The support sinters to 95% density and presents adequate mechanical strength, even for 0.2 mm foils of 100 cm$^2$. Fig. 2 shows a top view of the electrolyte film. A perfectly sintered structure is visible, consisting of 1-4 μm grains. Fig. 3 shows a fracture view of a cosintered element, which in this case carries an additional ceria layer (postfired at 1200°C). The backscattered electrons image distinguishes the dark grey NiO from the light grey YSZ particles. Both remain of small size (~1 μm) and nickel is well dispersed. From this interface structure, it can be guessed that YSZ percolating to a depth of a few grain layers within the anode, may participate in the electrochemical reaction and thus lower the anodic polarisation.

Cathode Performance

Nature and structure of the cathode highly influences the total cell performance. A series of cathodes was tested on the anode supports: stoichiometric La$_{0.86}$Sr$_{0.14}$MnO$_3$, composite YSZ-(La$_{0.8}$Sr$_{0.2}$)$_{0.9}$MnO$_3$, insitu La$_{0.5}$Sr$_{0.5}$Co$_3$ (LSC, porous) and sputtered La$_{0.5}$Sr$_{0.5}$Co$_3$ (LSC, dense). Results in terms of current-voltage-power curves are depicted in Fig. 4. A performance progression is indicated in the sequence of cathodes as just cited. Numerical data are summarised in Table I, i.e. power density at 0.6 V, ohmic and polarisation losses both at 1 A/cm$^2$, for 750°C. The simultaneous decrease in polarisation and ohmic loss with corresponding increase in power density is evident. This translates the effectiveness of the cathodic interface, from TPB behaviour (LSM) through some mixed conduction (LSM-YSZ composite) to higher mixed conduction (LSC). For the latter case, the combined structure of a thin dense layer with an unfired porous contact layer proved superior to only the porous structure. The surface reaction dominates the mixed conducting bulk (12), in the case of the sputtered nanolayer the whole electrolyte interface is used.

Individual overpotentials cannot be determined quantitatively on asymmetrical (i.e. electrode-supported) cells (13). Therefore only the sum of overpotentials was derived, and compared on Fig. 5 for several cases. Fig. 5 contains also the result of a cell carrying an additional ceria layer (see Fig. 3) and a LSCF-CYO composite cathode sintered at 1100°C/2h. This combination showed a somewhat better performance than the unsintered LSCF cathode, on zirconia. Summarised, it appears that the use of composite YSZ-LSM can halve the polarisation loss of stoichiometric LSM, and that the use of cobaltite(-ferrite) cathodes offer a gain of ≥ 100°C in operating temperature reduction compared to YSZ-LSM composites, even more when these cobaltite(-ferrite)
are themselves formulated into composites with ceria, on a ceria interface layer. Currently tests are ongoing to quantitatively characterize the individual cathode performances by using symmetrical cells with a reference electrode. This will allow, by comparison with Fig. 5, to assess only the anode support overpotential. At present it is seen that the sum of cathodic and anodic overpotential at 1 A/cm\(^2\) (800°C) can be 0.13V (Fig. 6). From separate impedance measurements, we estimated the anode interface resistance at 800°C and zero current, to 0.085 Ωcm\(^2\). Usually this figure drops at higher currents. We then estimate the support anode polarisation (800°C/1 Acm\(^{-2}\)) to probably better than 0.08 V, and so to a performance at least a factor 2 better than screenprinted anodes (Fig. 1).

**Ohmic Resistance**

Characteristic of supported cells is the abnormally high ohmic loss, when considering alone the electrolyte film thickness and the known bulk conductivity of 8YSZ as a function of temperature. We reported this before (3-5) and it is consistent with parallel observations in the literature (14,15). On numerous cell tests with modified cathodes, we consistently could not improve beyond an ohmic cell loss of 0.1 Ωcm\(^2\), regardless of operating temperature. This is still a factor of 3-5 above the expected value for 10 μm thin 8YSZ at 700-800°C. Fig. 6a plots the cell ohmic resistance for a case where identical cathodes on 8YSZ films of varying thickness (2 and 7 μm) were tested. This points to the existence of a residual resistance, of 0.1 Ωcm\(^2\), at “zero thickness”. One explanation is the inefficient use of available electrolyte surface, because of the electrode porosities. Fig. 6b illustrates that, for a mixed conducting cathode, the cell ohmic resistance steadily decreases with increasing current density. More area of the interfacial zone seems to be used by the mixed conductor as its ionic conductivity increases at higher current densities, which corroborates the mentioned interpretation of inefficient use of available electrolyte surface at low current and therefore the presence of important ohmic loss. Calculations regarding current constriction alone (4,16) fail to fully explain the result: it would require a very narrow TPB width and large interparticle distances incompatible with SEM observation of the electrode-electrolyte interfaces, before reaching current constriction effects that can explain a resistance increase by a factor of 5 or 10.

Another element of explanation may come from nickel diffusion from the anode into the thin YSZ electrolyte film during high temperature cofiring. Measurements carried out at Risø Laboratory, Danmark, (17), have demonstrated that 2 mole% Ni-doped 8YSZ, after reduction, shows only half the ionic conductivity of nickel free 8YSZ. Hence, a twofold increase in ohmic cell resistance could be accounted for by this observation. Finally, Horita et. al. (18) have shown, through \(^{18}\)O SIMS depth profiling at the reaction zone of a patterned LSM-YSZ interface, that active sites for oxygen reduction are distributed inhomogeneously along the TPBs. Hence, the TPBL by itself is not a sufficiently precise parameter, the really active area at the interface could actually be quite small. Even when using a dense cathode as we did (sputtered LSC), the observed cell ohmic drop remained a factor of 3 above the theoretical value. The major contribution to this ohmic loss should then primarily be located at the porous anode interface, and may originate from a certain penetration depth of the anodic reaction zone through the participation of percolating YSZ anode particles in the electrochemical reaction. This was suggested above from the microstructural evidence of Fig. 3.

In conclusion, it seems not possible to lower the ohmic drop well under 0.1 Ωcm\(^2\) with our present anode supported cells. On the other hand, this represents usually less than half of the polarisation losses, which thus remain dominating, often on the cathode side.
Efficiency

A cell of 100 cm² active area requires a fuel flow equivalent to 40 A or more, i.e. ≥ 300 ml/min of H₂. This size therefore allows for testing under realistic conditions of fuel conversion, even in a sealless arrangement as in our case. This was performed on upscaled anode support cells, using an insitu LSCF cathode on the zirconia thin film. Fig. 7 shows a result at 800°C, for a typical flow of 1.7 g H₂/h (340 ml/min) and 250 g/h of air, as would be the case for industrial kW stacks. No limitation is observed up to 85% fuel utilisation, and electrical efficiency reaches 36% at a power output of 21 W.

Fig. 8 demonstrates the capability of a diagnostics measurement (impedance spectroscopy) also on cells with 100 cm² active area. The Nyquist diagramme has been normalised to Ω cm², in reality therefore impedances of 7-20 mΩ were recorded. Fuel flow was varied as indicated in the figure. The second semicircle-like response clearly depends on this parameter and may, among others, be related to a gas conversion impedance (19). The ohmic loss in this particular arrangement appeared unusually high (0.7 Ω cm² instead of 0.2-0.3 Ω cm²) which for a large part explains the only moderate performance of the large cells, when compared to the smaller ones. Reasons have to be sought in current collection losses, much more exhibited with larger than with smaller cells. Moreover, no Pt mesh was used on the cathode side but rather a metallic interconnect plate. We are confident to substantially improve this cell performance to ≥ 30 W.

CONCLUSIONS

Thin 8YSZ electrolyte has been deposited on Ni-8YSZ anode support plates, up to 100 cm² in size, by aqueous tape casting and cosintering. The cell performance at reduced temperature is very dependent upon, and often limited by, the cathode behaviour. Over 0.8 W/cm² at 750°C, when using the most efficient cathodes, was obtained on small cells. Fuel utilisation up to 85% and electrical efficiency of 36% at 800°C was demonstrated on 100 cm² cells. With all cells, ohmic loss was much higher than expected from the thin electrolyte alone, the apparent lower limit being approximately 0.1 Ω cm². Elements of explanation are given by current constriction, nickel diffusion and inhomogeneous distribution of active sites. Because of the difference in microstructure, support anodes are electrochemically superior to screenprinted anodes, by an estimated factor of at least two (80 vs. 160 mV loss at 800°C and 1 A cm⁻²).

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Table I : Comparison of power output, ohmic and polarisation losses of anode support cells tested with various cathodes, at 750°C (displayed in Fig. 4).

| Cathode type     | Power density @0.6V (Wcm⁻²) | Ohmic loss at 1 Acm⁻² (Ωcm²) | Polarisation loss (V) ηₐ + ηₑ at 1 Acm⁻² |
|------------------|-----------------------------|------------------------------|------------------------------------------|
| LSM              | 0.33                        | 0.23                         | 0.64                                     |
| LSM-8YSZ         | 0.53                        | 0.14                         | 0.34                                     |
| LSC insitu (porous) | 0.72                      | 0.12                         | 0.22                                     |
| LSC dense (PVD)  | 0.84                        | 0.10                         | 0.17                                     |
Fig. 1: Current-overpotential of screenprinted Ni-YSZ and Ni-ZrO₂ cermet (sintered 1300°C/2h) on 8YSZ electrolyte, H₂ fuel.

Fig. 2: SEM of the surface of a thin 8YSZ electrolyte film (1-4 μm grains).
**Fig. 3:** Interface between thin electrolyte and anode support (backscattered electrons image). NiO is visible as dark grey particles. The top layer is an additional ceria-yttria coating.

**Fig. 4a:** Current-voltage output of anode support cells with various cathodes, at 750°C.

**Fig. 4a:** Power output of the same anode support cells with various cathodes, at 750°C.
Fig. 5: Overpotential comparison (anode + cathode) of anode support cells with various cathodes, at 700-800°C.

Fig. 6a: Total ohmic resistance of anode supported cell, as a function of electrolyte film thickness. LSCF insitu cathode.

Fig. 6b: Total ohmic resistance of anode supported cell, as a function of current density. LSCF insitu cathode.
Fig. 7: Voltage, fuel utilisation, power density and electrical yield as a function of current density for a 100 cm$^2$ disc cell. Fuel flow 1.7 g/h, air flow 250 g/h.

Fig. 8: Nyquist diagramme of impedance measurement on cell of 100 cm$^2$ active area. Total impedances range from 7 to 20 m$. Influence of fuel flow is shown.