DEVELOPMENT OF A STANDARD NI-YSZ CERMET ANODE FOR INTERMEDIATE TEMPERATURES

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Ni-YSZ cermet anodes were prepared from commercial NiO and coarse crushed YSZ powders. After firing at 1300°C on pretreated YSZ electrolyte sheets, they were tested for performance and stability at 700-900°C against regular LSM cathodes. The overpotential loss was reproducibly determined as 150 mV at 1Acm\(^{-2}\) and around 800°C. No degradation over testing periods of 400 h was observed. The impedance response at increasing current densities decreased markedly and featured an inductive loop at low frequencies. Power densities of the PENs of 0.35Wcm\(^{-2}\) at 800°C were recorded. Impregnation of the electrodes with metal catalysts increased this value to 0.48Wcm\(^{-2}\).

INTRODUCTION

Despite numerous developments of conventional Ni-YSZ cermet anodes for the use in YSZ-based SOFCs, no general strategy or recipe for fabricating the material has emerged. Several solutions appear possible and no consensus has been reached, for example, on even such a fundamental aspect as to which of the cermet starting powders - NiO or YSZ - should possess the larger average particle size (1). The majority of groups do seem to prefer fine NiO dispersed within a framework of non-shrinkable, larger YSZ particles, in order to achieve nickel percolation for electronic conduction as well as high triple phase boundary length (TPBL). A solution becoming more popular is to mix with NiO both large and small YSZ, where the latter promotes adhesion to the electrolyte and prevents Ni agglomeration to some extent (2,3). This last process is regarded as the main cause for degradation. Agreement exists (4,5) on the interpretation that mainly the TPBL determines the interface impedance and current-overpotential characteristic, though generation of adsorbed surface oxygen species, indispensable for the charge transfer, may proceed both at the TPB and on the YSZ within the cermet bulk (5,6).

In the present approach the said mixture of YSZ both larger and smaller than NiO is provided from one batch, featuring a broad particle size distribution, rather than from a bimodal powder as normally used (2,3).

Whereas Ni-YSZ is still mostly operated at 900-1000°C, we emphasized characterisation at lower temperatures (700-850°C). One aim is to demonstrate high power density at these temperatures with standard single cells using a self supporting electrolyte with regular LSM and Ni-cermet electrodes. A standard once established, modifications for improvement of performance and stability can be undertaken. One such modification is presented here, involving the impregnation of both sintered cathode and anode with catalytic quantities of Ag and Ru metals respectively. Ru has demonstrated excellent catalytic properties for the anode reaction (7,8) as well as sintering resistance. Even with the change of fuel from hydrogen to processed natural gas, Ni-YSZ studies will remain relevant because the material is best known and has proven functionality under methane steam reforming conditions (9,10). This will be especially true for Ru-
added Ni-cermet, Ru being an excellent steam reforming catalyst and resistant to carbon deposition (11).

**EXPERIMENTAL**

Standard 8YSZ Tosoh powder was tape cast with the slurry reported in (12). Square samples were sintered to dimensions of 30 x 30 x 0.12-0.18 mm at 1500°C. These samples were translucent, robust and highly dense. To promote adhesion and overpotential lowering of the electrodes, the sintered 8YSZ electrolyte tiles received a chemical etch in 10% HF solution. La0.65Sr0.3MnO3 cathode powder was prepared by the citrate route.

Commercial NiO (Koch Chemicals Ltd., UK) of appropriate 1-2 μm average size and narrow size distribution was selected (BET area : 1.36 m²g⁻¹). Larger NiO would result in a low TPBL, hence in poor performance. Smaller NiO, while yielding higher performance, is prone to agglomeration and requires homogeneous mixing with fine YSZ powder. We report on the latter approach separately in these Proceedings (13). Tosoh 8YSZ powder was pressed to pellets and fired at 1400°C. These were then crushed in a zirconia mortar with a zirconia pestle and wet sieved (ethanol) through a 25 μm sieve. This process yields the sought-after powder of broad size distribution (15-0.2 μm) averaging to 5.5 μm (BET area : 0.52 m²g⁻¹).

NiO and YSZ were mixed in a 56:44 weight ratio, corresponding to 40 vol% Ni in the cermet after reduction. This lies just above the limit of nickel percolation. The amount of Ni has to be kept as low as possible to minimize the problem of agglomeration during operation. Mixing is achieved by ultrasonicallyating the NiO-YSZ suspension in isopropanol-terpineol solvent, followed by addition of ethylcellulose polymer (Ethocel 45) and stirring on a hot plate, whereby the alcohol evaporates and the ethocel dissolves. This crude but efficient method allows to prepare screenprint slurries economically (a few grams) yet reliably.

Cathode screenprint pastes were prepared similarly. Several layers of the anode paste were printed (1 cm²) on the etched 8YSZ electrolyte samples, together with a reference point at 3 mm distance, and fired at 1300°C for 2 h. Cathode layers and reference point were printed symmetrically to the anode side on the opposite electrolyte face and fired at 1100°C. A pure Ni-felt was attached to the anode with the anode paste. On the cathode side, Pt grid was attached with the cathode paste. From these Ni and Pt current collectors, 10 cm Pt wires led outside the hottest oven zone, where they were extended to the oven exterior by thick Ag wires, connected to the Pt by flame welding. The total PEN element was eventually squeezed between 2 perforated alumina fiber cushions and inconel flanges with a gas tube inlet each. The samples were heated to typically 800°C in 3 h under an air flow of ~300 ml/min (cathode) and a H₂-H₂O (97:3) fuel flow of ~200 ml/min (anode). The temperature was monitored by a thermocouple squeezed in between the flanges 1 cm away from the electrolyte.

Cells were polarized at voltages between 0.4 and 0.7 V. To avoid Ni oxidation during the start-up phase of the cell, the potential difference between anode and anode reference electrodes was not allowed to exceed 300 mV. Current-voltage curves were taken at temperatures between 700 and 900°C using a Wenking potentiostat. The cathode
and anode overpotentials were monitored using the two reference electrodes. Important hysteresis between forward (from OCV) and backward (from short circuit) scans of the curves was common, the backward scans indicating higher current values. The current stabilisation time at individual voltage points could be considerable (several h). As a time saving compromise, results were recorded as forward scans in steps of 50 or 100 mV and allowing 5' stabilisation time. These values thus lay below the steady state currents, therefore the current- and power densities reported here represent underestimates.

Impedance measurements (Zahner Elektrik IM5d, Germany) were performed at OCV, under current load and at different temperatures. The frequency domain ranged from 50 kHz down to 1-0.01 Hz, depending on the cell conditions. Impedance measurements allowed to determine the ohmic drops at cathode and anode side, in order to construct current-overpotential curves. The observed ohmic drops were small, especially at the anode side (50 - 100 mΩ), lying close to the detection limit of the apparatus (30 mΩ). The real axis intersection at high frequencies was at times slightly distorted by an inductance originating from the wires. These aspects together with the fact that only pseudo steady state current values were recorded, account for some scatter observed in the current-overpotential curves, in particular at high current densities (> 1 Acm⁻²).

RESULTS

Ionic conductivity values of our 8YSZ electrolyte are displayed in Table I together with commercial 8YSZ tiles. These values are among the highest yet reported. Despite high sinterability, conductivity and good current-overpotential characteristic of our in-house developed cathode compared to commercial LSM powders, the considerable cathode loss at intermediate temperature limited the overall power density of our cells.

The best sintering temperature for the anode was determined as 1300°C. Adhesion is weak after firing at 1200°C, and NiO sintering is too pronounced at 1400°C, resulting in percolation decrease. Conductivities at room temperature of fired and reduced anodes were determined as ~1500 S/cm (sintered at 1300°C) and ~400 S/cm (1400°C). Lower sintering temperatures are preferred since one aim is to cofire the electrodes at 1250°C.

The first operation of the cell is of vital importance for the final power output. Initial performance is usually extremely poor, on the order of 30 mW/cm². Polarizing the cell at 0.4-0.5 V and a minimal current of ~100 mA/cm² initiates formation of both interfaces and results in a continuous current increase, rapid in the first few hours, than asymptotically towards its final value, often more than one order of magnitude above the initial one. Cells that failed to be "activated" this way were characterised by an anode of mediocre adhesion. Succesfully activated cells, conversely, showed anodes superiorly bonded to the electrolyte impossible to remove even by a cutter blade.

Examples of improved anode characteristics with time are visualized in Figs. 1 and 2. Fig. 1 shows the evolution of the anode current-overpotential characteristic between 3 h of operation (when the interface formation has already started) and 18 h, after which the performance is stable up to nearly 400 h of testing time. The impedance plot of Fig. 2 illustrates that even beyond the first day of operation the anode continues to improve, featuring a lower impedance after 290 h than after 27 h under polarisation. Stable conditions for most cells were typically reached within 1 to 3 days of operation.
Reproducibility in SOFC in general, but with Ni-cermet fabrication in particular, is one of the most important aspects. Anodes were therefore prepared from three different screenprinting ink batches. The outcome is presented in Figs.3-6. Fig.3 compares the current-overpotential characteristics of four anodes at temperatures around 800°C. Given the data point scatter as aforementioned as well as the temperature and age differences indicated in the caption, such reproducibility is satisfactory. Typically 150 mV is lost at 1 Acm⁻², comparing well with the performance of “good” cermets at 1000°C (14,15).

It is established by several workers (5,14) that the anodic branch of the Ni-cermet behaviour corresponds to a Butler-Volmer type equation of

\[ j = j_0 \exp \left( \frac{2F \eta}{RT} \right) \]  \hspace{1cm} [1]

where the exchange current density is independently determined by (14)

\[ j_0 = \frac{ART}{3FR_p} \] \hspace{1cm} [2]

(A : electrode area, Rp : interface polarisation as indicated in Fig. 2).

A best fit of equation [1] to the curves in Fig. 3 and 1, for a temperature of 800°C, is presented as a solid line in the figures. \( j_0 \) was found to amount to 30 mA/cm², corresponding with equation [2] to a Rp of ~1 \( \Omega \text{cm}^2 \), reasonably agreeing with the plots in Fig. 4. Despite the data scatter a consistency between fit and experiment is apparent.

Whereas the impedance response at OCV in Fig. 4 shows some degree of similarity between anodes originating from the same paste, the discrepancy between pastes can amount to a factor of two. Since the impedance response is very sensitive to morphological differences and fabrication origin of the anodes, as already clearly reported (16), Fig.4 does not present an inconsistency. Remarkable, conversely, is the reproducibility of the impedance behaviour under load, as presented in Figs.5 and 6. (Digits in the impedance plots indicate frequency powers of 10 in Hz.) At current densities of ~95 and ~220 mA.cm⁻², the responses of the three cells of Fig.4 virtually overlap. Since the Rp values of the plots in Figs.5 and 6 represent the slope of the overpotential-current curves, a verification is easily carried out employing the derivative of equation [1],

\[ \frac{\partial j}{\partial \eta} = j_0 \frac{2F}{RT} \exp \left( \frac{2F}{RT} \eta \right) \] \hspace{1cm} [3]

Using \( j_0 = 0.03 \) and calculating equation [3] at currents of 95 and 220 mA, values for Rp of 0.49 respectively 0.21 \( \Omega \text{cm}^2 \) result, agreeing very well with the measurements, thus further corroborating the validity of equation [1].

Figs.7 and 8 demonstrate the variation of the anode characteristic with temperature. The general shape remains constant in both figures and a rather important thermal activation is apparent. From Fig.8, an Arrhenius slope of 1.07 eV is derived. Extrapolation of the interface impedance to 1000°C results in a value of 0.17 \( \Omega \text{cm}^2 \),
coinciding very well with values for excellent cermet anodes reported by other workers (2,14). Also the activation energy is consistent with the literature (4,5).

Fig. 9 depicts the variation of the impedance spectrum of a representative anode with current load over a considerable range. The large polarisation resistance at OCV is drastically reduced as soon as current is passed through the cell. Granted that the reaction is governed by the TPBL and that therefore a constant interfacial area over the covered potential range applies, this behaviour clearly points to a charge transfer limitation, the more since the capacitance of this arc varies insignificantly with potential. Under load, the spectrum decouples from a semicircle to one with an additional inductive loop at low frequency. This behaviour indicates a reaction involving a concentration impedance of an intermediate adsorbate and the desorption of the formed product (17).

Mechanisms involving the dissociative adsorption of hydrogen as well as the generation of adsorbed surface oxygen species have been evoked (5,18), together with the combination step of both adsorbed hydrogen and oxygen species to give the product, H$_2$O(g). Elaborate work on the H$_2$/Ni-YSZ cermet reaction mechanism was reported by Mogensen (5,16,18). He found 2 to 3 time constants at OCV for all investigated anodes, depending on the $P_{H_2}$, $P_{H_2O}$ and microstructure. The high frequency arc (50 kHz-10 Hz) is dominating at "elevated" $P_{O_2}$ around 10$^{-17}$ atm (3% H$_2$O at 1000°C), whereas a low frequency arc (10 Hz-0.1 Hz) grows with lower $P_{O_2}$ (10$^{-20}$ atm, "dry" H$_2$). Simultaneously, the electrode reaction zone grows from a narrow interfacial layer (TPBL) into the electrode bulk. No fitting of the present data to equivalent circuits was yet attempted, but, from the frequency domain, our single arc response for "flooded" electrodes (gas flow excess) clearly corresponds to the dominating high frequency arc in 3% H$_2$O as reported by others (14,16). This reaction, involving a limiting charge transfer across the TPB, was ascribed to the surface species combination (5)

$$H^{+}_{ad,Ni(TPB)} + O^{2-}_{YSZ(TPB)} \rightarrow OH^{-}_{YSZ(TPB)}$$

or generally the formation of an adsorbed oxygen species at the YSZ interface. This Rp is directly related to the TPBL (4,5). Therefore, the smaller the nickel particles, the more favourable the anode current-overpotential characteristic (13).

The decoupled loop at low frequency (Fig.9) is then likely due to hydrogen adsorption to form the H$^+$ intermediate. Adsorbed H$^+$ on the nickel surface migrates to the TPB in order to react with the adsorbed oxygen species on YSZ.

Fig. 10 presents current-voltage data of standard cells developed in this work. Appreciable power of 0.35 Wcm$^{-2}$ was achieved at the comparatively low temperature of 795°C (2.5 Acm$^{-2}$ short circuit). The cathode was more limiting than the anode.

As one way of improving the output, the electrodes were impregnated with catalysts. In the porous, sintered cathode, AgNO$_3$ solution was infiltrated by brushing, leaving 1 mg of silver dispersed within the cathode after decomposition. In the porous, sintered anode, RuCl$_3$ solution was infiltrated by brushing, leaving 150 µg of Ru dispersed within the anode after decomposition. The cell was otherwise prepared and mounted in exactly the same way as a standard cell. The current-voltage data is displayed in Fig. 11. An improvement on both anode and cathode side was clearly observed, e.g. 100 mV anodic
overpotential at 1 A cm\(^{-2}\) and 800°C compared to 150 mV for regular Ni-YSZ. Maximum power increased consequently, for example from 0.35 to 0.48 W cm\(^{-2}\) at 796°C. Even at 700°C, these self supporting YSZ cells delivered 0.16 W cm\(^{-2}\). The power maxima together with the OCV's as a function of temperature for both the standard cell (Fig. 10) and improved cell (Fig. 11) are displayed in Table II. The low OCV's as evident from Table II were in part responsible for low power densities at the target voltage of 0.7 V. This was due to the use of small samples in a large, open flange system with free-flowing gases where excess H\(_2\) and air are reacted at the cell edge. An increase of 0.1 V in cell voltage employing larger samples will be possible. The current-voltage curves will be shifted upwards and power densities of 0.2, 0.5 and 1 W cm\(^{-2}\) at 700, 800 and 900°C respectively should lie within reach. Of course, these data apply to "flooded" electrodes. Nevertheless, such high values have to be demonstrated at low utilisation in order to achieve acceptable results at a projected higher fuel utilisation. As an example may serve the data published by ECN (19), where at 930°C 0.5 W cm\(^{-2}\) was achieved under excess flow conditions and 0.2 W cm\(^{-2}\) at 80% fuel utilisation.

### SUMMARY

Conventional Ni-YSZ has been developed showing good stability (400 h) and performance (150 mV loss at 1 A cm\(^{-2}\) and 800°C) at intermediate temperature. Further improvement was achieved by catalyst impregnation to give PEN power of 0.48 W cm\(^{-2}\) and 0.82 W cm\(^{-2}\) at 796°C and 892°C respectively. Characterisation of optimised cells in closed systems will be tested in future, to determine the effect of gas utilisation. Several anode modifications are now under investigation in our laboratories to further improve performance and long-term stability, and to elucidate the reaction mechanism.

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Table I: Ionic conductivity of our electrolyte compared to commercial samples

| Temperature | EPFL 8YSZ | Kerafol 8YSZ |
|-------------|-----------|-------------|
| 700°C       | 2.8       | 1.3 S/m     |
| 800°C       | 5.6       | 3.0 S/m     |

Table II: Power densities and OCV of standard and improved cells

| Temperature | Standard cell | Improved cell |
|-------------|---------------|---------------|
| OCV | Power | OCV | Power |
| 700°C | 1.01 V | 0.12 Wcm⁻² | 0.97 V | 0.16 Wcm⁻² |
| 750°C | 0.99 | 0.23 | 0.96 | 0.28 |
| 795°C | 0.98 | 0.35 | 0.94 | 0.48 |
| 840°C | 0.97 | 0.54 | 0.92 | 0.66 |
| 890°C | 0.91 | 0.66 | 0.91 | 0.82 |
Fig. 1 Anode characteristic of a cell operated for nearly 400h at 825°C, as a function of time.

Fig. 2 Evolution of the impedance response of the anode interface with time.

Fig. 3 Anode characteristic of anodes from several pastes. Cell1:825°C, 18h. Cell9:805°C, 169h. Cell15:821°C, 22h. Cell18:795°C, 39h.

Fig. 4 Comparison of anode impedance response for various cells at OCV and around 800°C.
Fig. 5
Impedance response of the cells of Fig. 4 at a current of around 100 mA. Series resistances were substracted.

Fig. 6
Impedance response of the cells of Fig. 4 at a current of around 220 mA. Series resistances were substracted.

Fig. 7
Anode overpotential (cell 18) as a function of temperature.

Fig. 8
Anode impedance (cell 18) as a function of temperature at OCV.
Evolution of the anode interface impedance with current. Scaling is different for the two graphs for clarity reasons.