THE MATERIALS AND TECHNOLOGY DEVELOPMENT OF CERAMIC COMPONENTS FOR A REDUCED TEMPERATURE SOFC

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ABSTRACT

The economics of SOFC power plants can be improved considerably by a reduction in the operation temperature of the fuel cell stack. At the same time the lifetimes of all the system components are distinctly extended. However this step presupposes intensive further development of those ceramic components which represent the electrochemically active parts of the SOFC. Alternative materials and fabrication technologies for fuel cells operating at reduced temperatures are discussed and preliminary results are presented. Single cells using conventional 8YSZ electrolyte substrates already deliver 0.35 W/cm² at 820 °C and, in continuous operation tests carried out at 0.15 W/cm², show no degradation in the cell voltage after more than 4000 hours.

INTRODUCTION

Until now the operation of a SOFC was based upon temperatures around 1000 °C. Such a high operating temperature offers the following advantages for the fuel cell itself and the plant:
- good electrode kinetics (low polarisation losses)
- high conductivities in the solid electrolyte (and in the ceramic interconnect)
- utilisation of the exhaust gases in a combined cycle.

The disadvantages against are:
- degradation of all components and interfaces via solid state diffusion
- corrosion of the metallic interconnect
- peripherals in the system which are temperature resistant are too expensive.

System studies have shown that a temperature interval of around 200 K is required between the inlet and exit temperature of the reactants for the economic operation of a SOFC stack. A gas inlet temperature of approximately 750 °C however...
leads to a drastic reduction in the stack performance due to higher losses in the electrochemically active single cells. It follows directly from this that there is a demand for more suitable materials or production technologies for these single cells.

**STATE OF THE ART TECHNOLOGY FOR SINGLE CELL ELEMENTS**

The single cells used to date consist of a self supporting electrolyte substrate (150 μm thick, substrate area 5x5 or 10x10 cm²) of cubic stabilized 8YSZ (Tosoh TZ8Y), which is covered on both sides with screen printed electrodes (30 to 50 μm thick, electrode area 4x4 or 9x9 cm²). A two component cermet of Ni(O) and 8YSZ is employed as a starting material for the anode. For the cathode, a stoichiometric perovskite of the composition La₀.₈Sr₀.₂Mn₀₃ is used. The preparation of the electrode materials is carried out conventionally via solid state reaction between the oxide/carbonates of the relevant cations.

These single cells deliver at an operating temperature of 950 °C sufficient current density (between 0.9 and 1.1 A/cm² at a cell voltage of 0.7 Volt in O₂ vs. H₂, average fuel utilisation ≤ 15%), see figure 1. The long term performance of these cells is at present unsatisfactory; the change in the cell voltage is 3% and 1% respectively per 1000 h at a power loading of 0.3 W/cm², see figure 2. Results and measurements on state of the art single cells and stacks are further discussed in [1].

With a reduction in the operating temperature of about 130 K, the current density of the cells is already diminished due to an increase in electrical losses in the components by about 70 %, though the degradation of the cell voltage over a period of 4000 h is no longer a problem (see figures 3 and 4).

**THE MATERIALS AND TECHNOLOGY DEVELOPMENT FOR A REDUCED TEMPERATURE SOFC**

If the SOFC is run using a temperature interval of 200 K, then with a maximum exit temperature of 950 °C, the inlet temperature of the fuel is lowered to 750 °C. The losses in the electrochemically active single cells can be estimated for anode, cathode and electrolyte as shown in figure 5 (polarisation and ohmic losses for the anode and cathode, ohmic for the electrolyte). By considering these points the following areas for development are identified for the components and also for materials combinations in a single cell:

- Improvement of electrode kinetics at a reduced operating temperature. As figure 5 shows, it is particularly relevant to minimize the cathodic losses. This can be achieved either by an increase in the three phase boundary between the electrode/electrolyte/gas, or by the use of mixed conducting cathodes and/or
electrolyte layers. The same considerations are valid for the anode, though of comparatively lesser importance.

- Minimization of ohmic losses for reduced operating temperatures. Figure 5 shows that this requirement is applicable particularly to the electrolyte (and to the ceramic interconnect). This can be achieved by the use of sufficiently thin electrolyte membranes of 8YSZ or by the use of an alternative electrolyte material with a higher ionic conductivity/mechanical stability.

- Concentration on the mechanical stability of single cells. In the case of a thin electrolyte membrane of 8YSZ, this means combination with thick electrodes (anode and/or cathode). For alternative electrolyte materials it implies a self supporting substrate with compatible or superior mechanical properties than 8 YSZ.

- Low degradation in the entire temperature interval is obviously essential (target value of $\Delta V/V \leq 0.5\%/1000$ h). This requires for all electrical and electrocatalytical active sites a minimisation of the diffusional processes, especially by the stabilisation of the electrocatalytically active sites.

We aim to increase the performance, long term stability and mechanical stability not only of our state of the art single cells but also for the development of alternative materials and technologies. Preliminary results are presented in the following chapters.

**Further development of the cathode**

An improvement of the electrochemical half reaction of the cathodic side has been the aim of numerous researchers [i.e. 2,3,4,5,6,7,8,9]. For the cathode material the main routes of achieving this are:

- Use of cathodes with an ionic conductivity component which is achieved by substitution of Co or Fe for Mn, for example.
- Increase of three phase boundary at the cathode/electrolyte/gas interface, e.g. by tailoring the grain size of cathodes, by the addition of YSZ to the cathode material or by the texturing of the electrolyte surface.
- Surface doping of the electrolyte to produce partial electronic conductivity.
- Avoidance of secondary phases by sub-stoichiometric (La-deficient) cathode compositions or by thin buffer layers [10], which prevent the reaction between cathode and electrolyte.

Some investigations on mixed conducting cathode materials (substitution of Co for Mn) have been reported by various authors already and have shown that in principal a reduction in the polarisation losses at the cathode is possible (see figures 6 and 7 from [8]). However for practical application, a reduction in the cofiring temperature for both electrodes is required on account of the intense reactions, which produce secondary phases. Furthermore consideration of the stresses at the interface, which are brought about by the distinctly higher thermal expansion coefficient of the cobalt containing cathodes, can lead to the detachment of the cathode from the electrolyte when the cell is...
thermally cycled. This can be alleviated by a very thin electrode layer or by the addition of YSZ, for example, to the cathode.

The increase in the three phase boundary by using a tailored microstructure, which was made from chemically prepared raw materials (development: Rhone Poulenc, France, and SSC, Canada) produced up to date no improvement. In particular the operation of cells in air resulted in a higher drop in the performance, for which, this is suggested, the hindering of gas diffusion in the fine pore microstructure is responsible. A further development in the performance is possible here, but for the fine grained cathode this requires the specific optimisation of the microstructure with respect to the porosity and lateral conductivity. As the costs for such starting materials are to date considerably higher (by a factor of ≥ 10 compared to the conventional solid state reaction process), this route does not seem to be very sensible.

Secondary phases at the interface have a considerable effect on the electrode kinetics, being especially disruptive at lower temperatures. As the stoichiometric composition can result in the formation of a secondary phase layer [11], the lanthanum content in the cathode material was varied. For the stoichiometric cathode the TEM investigations reveal a La2Zr2O7 layer around 20 to 100 nm thickness at the interface at electrode cofiring temperatures ≥ 1300 °C. At a lower operating temperature of 820 °C the lanthanum-deficient cathode attained a current density of 0.5 A/cm² at a cell voltage of 0.7 Volt, while the stoichiometric cathode only achieved 0.3 A/cm², as the I/V characteristics in figure 3 show. TEM carried out on both cells after operation showed that for the substoichiometric cathode no secondary phases formed at the interface, although a slightly increased diffusion of Mn into the topmost grains of the electrolyte did result. The better performance could therefore be attributed to a change of the electrical properties within the electrolyte/electrode interface as well [12].

Further development of the electrolyte

In the planar concept the electrolyte is employed as a self supporting substrate and for large area electrolytes (≥ 100 to ≤ 400 cm²) even a thickness approaching 300 μm seem to be necessary for practical handling. The 8YSZ electrolyte we use in our single cells has an area of 25 cm² and a thickness of 150 μm. The total losses in the single cell increase with decreasing temperature and become predominantly due to the electrolyte (besides the cathode, as discussed above) because of the temperature dependant ionic conductivity. Figure 5 shows the increase in the (calculated) electrolyte losses from 147 mΩcm² at 950 °C to 468 mΩcm² at 820 °C corresponding to a current density of 0.3 A/cm². This proportion of the total losses can be reduced by:

- a reduction in the electrolyte thickness of 8 YSZ [14] or alternative materials whose $\sigma_{\text{ion}} \leq 8YSZ$.
- the use of alternative materials with $\sigma_{\text{ion}} \gg 8YSZ$ [15].
The mechanical properties (fracture strength and fracture toughness) of the relevant material are essential, since in the planar concept the electrolyte is employed as self supporting substrate. The following alternatives to the current set up can be considered:

- For 8 YSZ (and comparable dopant concentrations) the thickness has to be reduced to ≤ 50 µm. At this thickness the electrolyte can no longer function as a self supporting substrate, as the mechanical stability of 8 YSZ is insufficient. Therefore one or both of the electrodes must act as the support.

- TZP substrates of comparable thickness display considerably better mechanical properties [13]. At lower temperatures the ionic conductivity of TZP is equal to 8YSZ (see figure 8). Self supporting substrates of TZP (thickness about 50 µm) are already possible and should be able to replace 8YSZ. Nevertheless mechanical properties (degradation of strengthening mechanism in water vapor at elevated temperatures) and long term stability must be proven under operating conditions.

- An electrolyte material with σ_{ion}>> 8YSZ can be used as a self supporting substrate of 150 to 200 µm thickness even at lower operating temperatures. Gadolinium doped Ceria (GCO) seems to be a promising candidate at temperatures below 750 °C. In order to successfully replace 8YSZ, the single cell with a self supporting GCO substrate should possess sufficient mechanical properties, long term stability and compatible electrode materials.

Electrolyte development is an important research activity for many groups. Our own work, which is intensively supported by national and european partners, has attempted to investigate these materials and technologies in parallel.

For Gd-doped Ceria the effect of doping concentration on sintering behaviour and electrical properties was investigated as well as various raw materials sources (development: Rhone Poulenc, France and SSC, Canada). A deagglomeration step made it possible to achieve high density ρ (≥ 98 ρ_{theor.}) by sintering at 1550 °C. The various GCO samples show minor differences in conductivity depending on dopant concentration and fabrication route. The best sample (GCO20 with 20 at% Gd in CeO₂, SSC) possesses a value of σ = 6.4 S/m at 750 °C in oxygen, which is 5 times better than 8YSZ and 6 times better than TZP. The conductivity measurements as a function of temperature and oxygen partial pressure are illustrated in figures 8 and 9.

The preparation of substrates and two or three layer laminates for application in single cells is being pursued in a european development programme. The first cells with a GDC substrate have already been successfully tested, and single cells with improved electrodes already display a current density of about 0.5 A/cm² at a cell voltage of 0.7 Volt at 700°C [16].

The self supporting substrate of TZP (thickness 100 µm) had electrodes screen printed on before testing. A lanthanum deficient composition has also been used as a cathode material. Figure 10 shows the I/V characteristics of the 8YSZ (150 µm thick)
and TZP (100 μm thick) single cells at 800, 820 and 950 °C. The electrodes for both cells are identical. At 950 °C the cells display considerable difference in the development of the I/V characteristic which is due to the higher resistance of the TZP electrolyte. With a reduction in the operating temperature the two cells approach one another. Even thinner substrates of TZP could therefore offer an advantage, but this is of course subject to long term performance under operating conditions. The preparation of two layer laminates for the production of a coating layer on TZP is also investigated in our european consortium.

Laminated three layer single cells (IPEN: Integrated PEN structure, PEN: Positive electrode/Electrolyte/Negative electrode) were produced by cofiring our state of the art electrolyte and tape casted electrode materials (green tape thickness of 200 and 80 μm respectively). In order to accomplish this, the shrinkage behaviour of the individual components were adapted to one another, the green tapes were laminated under temperature and pressure and finally sintered at a temperature of 1350 °C. We were able to sinter up to 4x4 cm² three layer laminates free of cracks or delamination effects. The I/V characteristics of these very first IPENs are shown in figure 11. Current density of about 0.7 A/cm² at 0.7 Volt and 950 °C and about 0.5 A/cm² at 850 °C is in good agreement with our state of the art single cells. Nevertheless, it has to be pointed out, that the IPENs were characterized by "flooding" the electrodes with gases, that means without any gas utilization. Variation of the thickness of the various layers and adaptation of the materials/technology should lead to a further improvement at lower temperatures. The IPEN with custom tailored layer thicknesses/microstructures for electrolyte and electrodes is an important development aim of our european consortium.

CONCLUSIONS

The results presented here detail the numerous possibilities for the improvement of single cells for reduced operating temperature. At the present time it is not yet apparent which combination of materials and technologies is the most promising. Alternative materials and interfaces must be tested for long term stability under realistic operating conditions, before they can replace the current single cells in the stack. For this development it is essential to keep in mind the costs of the alternative materials and technologies, in order to further guarantee the economics.

ACKNOWLEDGEMENTS

Since January 1994 this research program is funded by the european community (Brite/Euram BRE2-0578/Project no. 7582) and the german ministry of research and technology (BMFT/PLR contract no. 03M27478). We like to thank all our national and
European partners for their good collaboration and our colleagues for their intensive support by means of X-ray diffractometry, microprobe analysis, chemical analysis and TEM investigations. We express our thanks to Roger de Souza for his help in translation.

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Fig. 1: Current/voltage characteristics of state of the art single cells at 950°C (0.5 l/min H₂ - 0.5 l/min O₂).

Fig. 2: Long term degradation of state of the art single cells at 950°C (0.5 l/min H₂ - 0.5 l/min O₂).

Fig. 3: Current/voltage characteristics of state of the art and improved single cells at 820°C (0.5 l/min H₂ - 0.5 l/min O₂).

Fig. 4: Long term degradation of state of the art single cells at 820°C (0.5 l/min H₂ - 0.5 l/min O₂).
Fig. 6: Potential drop at a La$_{0.8}$Sr$_{0.2}$MnO$_3$ cathode as a function of firing and operation temperature (see [8]).

Fig. 7: Potential drop at a La$_{0.8}$Sr$_{0.2}$MnO$_3$ cathode as a function of firing and operation temperature (see [8]).

Fig. 5: Resistances due to polarization and ohmic losses of single cell components as a function of temperature (Current density $j = 0.3$ A/cm$^2$).
Fig. 10: Current/voltage characteristics of single cells with 8YSZ (150 μm) and TZP (100 μm) in 250 μm electrode area (0.5 mm/min H2 - 0.5 mm/min O2)

Fig. 11: Current/voltage characteristics of a co-fired integrated PEN (electrolyte: 150 μm, electrodes 50 μm electrode area: 0.95 cm2)