HOLLOW ELECTRODE LOOSE PLATE SOFC DESIGN

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ABSTRACT

A novel planar SOFC design is presented, based on the loose stacking of hollow electrode elements, conventional plate type electrolytes and interconnectors. This facilitates free thermal expansion during operation, and thermal cycling, thereby significantly improving prospects for reliable SOFC operation in power generation practice. Each individual element only consists of one material, eliminating the need for sealing and for matching thermal expansion coefficients of fuel cell components. Application of hollow electrodes results in an inherent manifolding of the gas streams eliminating the need for seals at the fuel cell stack itself. The design has been tested at laboratory scale and a small working prototype fuel cell has been successfully tested.

INTRODUCTION

Planar high temperature SOFC's offer many advantages for power generation, the most important being compactness and the resulting high power per volume ratio. However, current designs consist mainly of sintered monolithic cells giving rise to problems related to thermal stress. The large temperature interval between start-up and operation can cause significant expansions despite only a slight difference in thermal expansion coefficients. The manifold boards at the boundaries of the cell are also subject to leaking problems due to differences in thermal expansion. In addition, the thermal gradient in the materials itself create thermal stress especially at discontinuities like edges, adhesion zones, and seals.
Why another design?

Ceramic materials like SOFC materials show relatively low critical tensile stresses compared to their critical compressive stresses resulting in brittleness. Therefore, a major concern is to prevent leakage at connections, adhesions, and seals of ceramic components. Leakage in an SOFC can cause reduced efficiency, more importantly may greatly reduce reliability, and even cause danger when oxidant and fuel gases come in direct contact with each other. The mechanical problems of an SOFC should be reduced as much as possible in order to enable the optimization of the electrical output of the SOFC.

In order to minimize the ohmic losses of an SOFC the electrical properties of the components need to be improved. Besides, the thickness of the component layers should be minimal, yet mechanically stable. For some state-of-the-art SOFC materials the specific resistivities are plotted in Figure 1.

Because the oxidant and fuel gases have to be separated by the electrolyte and interconnect materials, a certain minimum thickness is necessary. Besides their electrochemical use a certain minimum thickness has to ensure the gastight separation of the oxidant and fuel gases. It is rather unfortunate that this function is provided by the two least conductive materials. These materials need also to be resistant towards both an oxidizing as well as a reducing atmosphere at high temperatures. This significantly restricts the selection of the materials for utilisation in an SOFC.

To minimize or eliminate the above mentioned problems related to current SOFC's a novel SOFC design is presented. Earlier designs have been based on increase of surface area, decrease of conduction pathway, or the counter-current flow of oxidizing and fuel gases (honeycomb design). However, the present design can be regarded as more fundamental.

To reduce or eliminate mechanical stresses due to different thermal expansion coefficients (TEC) three solutions can be envisaged, i.e.

1. Matching of TEC's and intimate contacts
2. Less types of material and intimate contacts
3. Stacking and loose contacts of components

To date SOFC engineering is focused on the matching of the TEC's to the YSZ electrolyte material by optimizing material composition and by doping (e.g. the amount of Sr doping in La$_{1-x}$Sr$_x$MnO$_{3+y}$ cathode material).
The second concept is described in US patent 5,330,859 of July 1994 [ref.1]. Here a monolithic SOFC is described consisting of only two types of material. Besides a conventional YSZ planar electrolyte, $La_{0.6}Sr_{0.4}CrO_3$ is used as interconnect as well as both cathode and anode. This approach reduces the number of materials of which the thermal expansion coefficients need to be matched. However, this can be regarded as a sub-optimal approach, as it is not specifically designed for use in both anodes and cathodes, but merely as interconnect material. It is expected that the use of one material as interconnect, anode and cathode will result in increased reliability at the cost of reduced performance.

**THE NOVEL HELP DESIGN**

The principle of the novel design is based on the loose stacking of fuel cell elements in combination with hollow gastight electrodes (Hollow Electrode Loose Plate concept) [ref.2], see figure 2.

Hence, this type of SOFC does not exhibit the problems related to the production and operation of monolithic SOFC's. This allows for mono-material production of fuel cell elements without sintering for adhesion purposes. When thermal cycling during operation the expansion of the elements can occur individually and freely so very little thermal stress will be subjected to neighbouring elements.

**Electrochemistry of the HELP design**

At the operating temperature oxygen is reduced at a two-phase contact zone, and transport of resulting oxygen ions and electronic charge carriers can take place through the dense mixed conducting electrode layer towards the solid electrolyte, i.e. figure 3.

In this design it is assumed that oxygen will not be present at the electrode-electrolyte interface in the gaseous state but exclusively as oxygen ions. Therefore, the solid electrolyte need not be gastight, which allows for the use of a thinner electrolyte, thus enabling a reduction of ohmic losses and hence a lower operating temperature.

Oxygen ions enter the mixed conducting hollow anode, and react internally with the fuel gases, see figure 4.

The utilisation of a thin film gastight mixed conducting cathode has already been suggested. However, this concept was not yet tested in combination with loose stacking of fuel cell elements as in the HELP design.
EXPERIMENTAL RESULTS

A recent feasibility study of the HELP concept [ref.3] revealed the potential of the present design. La_{0.85}Sr_{0.15}MnO_3 disks (D ≈ 2 cm) were sintered to full density from commercially available powder (Gimex). In the centre at one side a cavity was made resulting in a gastight hollow electrode.

The following cells have been studied using impedance spectroscopy in order to obtain information on the resistances of loose contacts and possible improvements:

\[
\begin{align*}
&\text{O}_2/\text{Pt} \mid \text{YSZ} \mid \text{Pt}/\text{O}_2 \\
&\text{O}_2/\text{Pt} \mid \text{YSZ} \mid \text{YSZ} \mid \text{Pt}/\text{O}_2 \\
&\text{O}_2/\text{Pt} \mid \text{YSZ} \mid \text{YSZ powder} \mid \text{YSZ} \mid \text{Pt}/\text{O}_2 \\
&\text{O}_2/\text{Pt} \mid \text{YSZ} \mid \text{YSZ paste} \mid \text{YSZ} \mid \text{Pt}/\text{O}_2
\end{align*}
\]

The results of the conductivity measurements are exhibited in figure 4.

The conductivity results with powder and particularly paste application show that loose contacts can be optimized such that their use in an SOFC seems a viable option.

To assess the functionality of a loosely stacked hollow electrode, La_{0.85}Sr_{0.15}MnO_3 disks (D ≈ 2 cm) were sintered to full density from commercially available powder (Gimex). In the centre at one side a cavity was made resulting in a gastight hollow electrode. This LSM disk has been tested under fuel cell conditions.

The DC characteristics of the (fuel) cell:

\[
\text{O}_2/\text{LSM} \mid \text{YSZ} \mid \text{Pt}/\text{H}_2
\]

has been experimentally determined, where LSM is a hollow gastight electrode, viz. figure 6 for a schematic view of the cell.

A typical I/V characteristic is presented in figure 7, showing the feasibility of the concept. The observed OCV was in good agreement with the theoretical value.

MANIFOLDING

Besides the new cell concept the manifold design has been adapted to the present SOFC design. It is schematically presented in figure 8 and comprises gas pipes, which can move relatively freely, due to the application of a viscous glass seal [ref.4]. A variety of borosilicate based types of material have been suggested for the sealing.
CONCLUSIONS

The concept of loose stacking and hollow gastight electrodes to construct an SOFC seems attractive. In comparison to conventional SOFC behaviour the results from the present feasibility study are very promising. Further research is aimed towards optimizing the HELP design.

REFERENCES

1 U.S. Patent 5,330,859 (1994), Solid oxide fuel cell with single material for electrodes and interconnect.

2 U.S. Patent pending (1994), Hollow electrode for an electrochemical cell provided with at least one inlet and one outlet opening for gases, and also electrochemical cell which contains such an electrode.

3 J.A.M. van Roosmalen, K.H. Plaisier, and J. Schoonman, Feasibility study on the HELP SOFC design, Laboratory for Applied Inorganic Chemistry, Delft University of Technology, Delft, The Netherlands (1994)

4 U.S. Patent 5,360,681 (1994), Seals for gas-carrying lines and installations which comprise such seals.
Figure 1: Temperature dependence of the specific resistivity of the state-of-the-art SOFC components.

Figure 2: Schematic view of the principle of loose stacking of HELP SOFC elements showing the ability of free expansion in the X-Y plane.

Figure 3: Schematic drawing of a functionally graded HELP cathode. The function of the electrocatalytic layer (black particles) is to transform oxygen molecules from the gas phase to oxygen ions in the solid state. On top of the electrocatalytic layer is the dense top layer, which will be in contact with the electrolyte and transports the oxygen ions to the electrolyte. At the right-hand side of the drawing the role of the various layers is presented schematically.
Figure 4: Assumed working principle of the HELP SOFC. Both anode and cathode materials are mixed conductors.

Figure 5: Results of the conductivity measurements on several types of cells. Curve 1 represents data from a single electrolyte pellet. Curve 2 presents data for two flat electrolyte pellets pressed against each other. Curve 3: a ceramic electrolyte paste is applied between the electrolyte pellets. Curve 4 presents data obtained when an electrolyte powder is applied between the electrolyte pellets.
Figure 6: Schematic view of the experimental set-up of the hollow electrode under fuel cell conditions.

Figure 7: $1/V$ characteristic of a fuel cell constructed of a hollow $La_{0.6}Sr_{0.4}MnO_3$ cathode, a dense electrolyte, and a platinum anode, with an electrolyte paste between cathode and electrolyte. The operating temperature is 1223 K.

Figure 8: Manifold design for free movable gas pipes (1) of hollow SOFC electrodes using a viscous glass seal (2).