

INTERNATIONAL ENERGY AGENCY

Programme of R, D & D on Advanced Fuel Cells Annex II : Modelling & Evaluation of Advanced SOFC

# EF Nr. 192851

**Final report** 

# SOFC MICROMODELLING



Swiss Federal Office of Energy, Operating Agent Task II Berne, May 1992

## **PREFACE:**

## THE IEA PROGRAMME OF R, D & D ON ADVANCED FUEL CELLS

## International Energy Agency

The International Energy Agency was formed in November 1974 to establish cooperation among a number of industrialized countries in the vital area of energy policy. It is an autonomous body within the framework of the Organization of Economic Cooperation and Development (OECD). Twenty-two countries are presently members, with the Commission of the European Communities also participating in the work of the IEA under a special arrangement.

## Programme of R,D&D on Advanced Fuel Cells

The IEA Implementing Agreement for a Programme of R,D&D on Advanced Fuel Cells was established in April 1990 and comprised initially two annexes. One dealt with the analysis of the Balance-of-Plant of Molten Carbonate Fuel Cells and the other with the Modelling and Evaluation of Advanced Solid Oxide Fuel Cells. There are now ten signatories to the agreement: Denmark (DEA), Germany (KFA-Jülich on behalf of BMFT), Italy (ENEA), Japan (NEDO), the Netherlands (NOVEM), Norway (NCSIR), Spain (Hidroeléctrica Espa~nola), Sweden (NEA), Switzerland (OFEN), United Kingdom (DOE).

## Annex II: Modelling and Evaluation of Advanced Solid Oxide Fuel Cells

The collaborative effort was scheduled for an initial two year term of Annex II, with Switzerland acting as Operating Agent. The targeted objective was to advance natural gas-fuelled solid oxide fuel cells technologies through:

i) the numerical modelling of innovative concepts which have the potential for low-cost mass production and higher conversion efficiency; the establishment of the necessary experimental data base and the model validation;

ii) the elaboration of recommended practices for SOFC products evaluation and their application to available SOFCs in order to assist the development taking place in industry, strengthen confidence and prevent confusion in the market.

The original signatories were Italy, Japan, the Netherlands, Norway, and Switzerland. They have been joined by the United Kingdom, Denmark and Germany.

The task-sharing work has been divided into seven activities, each with an appointed activity leader:

- i) Stack Design Tool (Norway)
- ii) Micromodelling (Switzerland)
- *iii)* SOFC Data (Denmark)
- iv) Recommended Practices for Electrochemical Evaluation (United Kingdom)
- v) Recommended Practices for Thermomechanical Evaluation (Italy)
- vi) Recommended Practices for Powder Characterisation (The Netherlands)
- vii) Recommended Practices for Stack Evaluation (Japan)

Augustin McEvoy, from the Federal Institute of Technology, in Lausanne, acted as Operating Agent on behalf of the Swiss Federal Office of Energy.

## **Final report**

# SOFC MICROMODELLING

Activity leader : Switzerland

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## 1. Executive Summary

## I. Introduction

It is generally admitted that the electrochemical performance and life-time of SOFC single elements, the so-called **PEN** -structures (i.e.: Positive air electrode / Electrolyte / Negative fuel electrode) currently available are not yet satisfactory in order to build a complete SOFC system which would meet market requirements. It is also clear that the ohmic drop is no longer the major source of energy loss. Significant gains are now expected on electrode overpotential reduction. In this regard, the outstanding results obtained recently at Osaka Gas on a 1x1 cm PEN structure have provided a scale of reference for those expectations and thereby shown how much electrode development is a rewarding research activity.

During the IEA SOFC Workshop at Hertenstein, Switzerland, in June 1990, it was recognized that no comprehensive micromodel simulating the fundamental barriers encountered within a single SOFC PEN was available in order to avoid costly and time-consuming trial & error development. A collaborative activity on SOFC Micromodelling was therefore set up and implemented within the IEA SOFC Task and fruitful discussions were initiated during the Oslo IEA SOFC Workshop, in August 1991 among the group of participants, chaired by Helmut Tannenberger (Switzerland).

## **II. PEN modelling**

On the basis of the data found in the literature, the regular PEN behaviour can be modelled straightforwardly. Basic assumptions are:

- i) the electrolyte is a pure resistance,
- ii) each electrode is a resistance in parallel with a capacitance (this assumption is indeed, as a first approximation, supported by many impedance observations). The knowledge of the capacitive electrode component allows one to model transient behaviour down to the millisecond scale,
- iii) the relative variation laws, as functions of the overpotential and of the electroactive gas pressures within the range of acceptable voltages are usually simple (respectively logarithmic and power laws for the electrode resistances),
- iv) the relevant activation energies can easily be measured,
- v) sufficient data is available. This data should allow one to model the electrochemical behaviour of a PEN as function of the current density, the fuel and comburant exhaustions and the local temperature variations,
- vi) *last but not least*, the numerical modelling of the behaviour of a PEN built out of any given new electrodes, could produce the expected information within a year, in any laboratory specialised in high temperature solid state electrochemistry.

## III. Electrode modelling

The contrast between the great simplicity of the observed electrode behaviour and the complexity of the electrode modelling is rather unpalatable in many respects. As stressed above, for general SOFC modelling, a straightforward model can be written on an empirical basis, refering to the observed variation laws, which are fortunately rather simple. On the other hand the devising of a comprehensive micromodel for the electrodes, tackling the fundamental barriers, which is crucial for the development of better electrodes, should not be, on the short term, expected to reach a sufficient reliability to serve as input for the modelling of a SOFC stack. Fortunately, as seen in § II, such a micromodel *is not essential to the general modelling of SOFC*. Therefore, the micromodel sought in this subtask can be entirely devoted to electrode development.

## **Basic Flow-charts**

The good old three phase boundary or triple contact line concept has been used since 1965(!). Hence, in order to bring some fresh air into the discussion (see Fig.1) and to allow a more accurate classification of the new results on mixed conductors, we will use *flow charts* as proposed by M. Kleitz.

The main AB line is the path followed by the *chemical species*. As an example, molecular oxygen,  $O_2$ , is represented in the gas phase at A, yielding the reduced oxide ion,  $O^{2^-}$ , at B.

The secondary CD line is the electron path.

Electric losses (ohmic drops and overpotentials) occur along the DCB line.

*Chemical losses* (decrease in chemical activities of the electroactive species, which can be converted into concentration overpotentials) occur along the AC line.

Both the main and the secondary lines can have branches, e.g., gaseous oxygen molecules can follow two competitive paths before reduction to oxide ions, but for the sake of simplicity we will ignore this possibility here.

## **Electrode categories**

Two types of electrodes can be identified, the classical "metal-like" triple contact electrodes, and the modern mixed conduction electrodes.

## *i)* the triple contact electrode

This kind of pure electronic conductor, "metal-like" electrode is characterized by a sharp transition in C between the electronic and the ionic conduction (see Fig.2). Its behaviour has been summarized above. Surprisingly enough, all reported materials which belong to this category do behave in the same way, i.e.: as first approximation, the electric behaviour is equivalent to an RC parallel circuit.

Quite obviously, the main parameter which should be increased in order to improve the reaction rate is the length of the triple contact line at the *electrode/electrolyte* interface. It depends on the average grain size of the electrode material and its porosity, as well as the roughness of the electrolyte surface. On the other hand, the thickness of such a porous electrode should not be a relevant parameter in terms of overpotential.





Fig.2: Flow-chart for a metal-like triple contact electrode









The use of composites made of co-sintered electrode and electrolyte powders are supposed to markedly lengthen the triple contact line. In this case, a thicker electrode should be favorable.

The nature of the electrode material certainly is another important parameter because of its catalytic properties, but one has to recognize that up to now, no new material has brought about a breakthrough in electrochemical performance. Their interest comes from other factors such as their low cost, longer life, or chemical and thermal compatibility.

## ii) mixed conduction electrode

It seems useful to define two main sub-categories of mixed conduction electrodes, depending on whether the mixed conduction material belongs to the electrode or to an electrolyte sub-layer which has been electronically doped.

- mixed conduction electrode: this case is described in Fig.3. The transition in C is continuous because of the extension of the ionic conduction into the electrode material. This is typically the case of the LSM air-electrode in its reduced state.
- mixed conduction sub-layer: this case is described in Fig.4. The transition in C is also continuous, but is due to the extension of the electronic conduction zone inside the electrolyte. This is typically the case of the Ni/YSZ-CeO<sub>2</sub> fuel electrode.

Under certain circumstances, the mixed conduction electrodes exhibit very small overpotentials (up to 10 or even 100 times smaller than those of conventional electrodes). The shape of their impedance diagram is usually more complex and often exhibits a Warburg component, indicating that a diffusion process plays a significant role.

For mixed conduction electrodes, the key parameter is the area of the surface exposed to the electroactive gas ( to oxygen, at the positive electrode) in the zone where the transition C occurs. A rather expanded, thick, porous electrode or a coarse electrolyte surface should exhibit better performance.

## Chemical energy losses : diffusion and absorption

The electroactive gaseous species diffuse from */to* the gas stream and through the pores of the electrode before reaching */after leaving* the sorbing active reaction sites. It may also diffuse on the sorbing surface. Depending on the rate of these processes, the local chemical activities of these species at the active electrochemical sites, might be different from their values in the gas stream. This would result in a lowering of the PEN voltage (concentration overpotentials). Refering to experimental observations, one generally assumes that diffusion in the gas phase, including diffusion in the pores, does not contribute to a significant overpotential. On the other hand, adsorption deserves more attention than usually paid; it is certainly an important source of overpotential.

From a physical point of view, it is obvious that with very small pore diameters, diffusion in the pores will become the limiting factor. It is therefore important to set experimentally and theoretically the limit for the pore diameters, a limit where diffusion overpotential becomes significant.

For adsorbtion */desorption*, the characterization of the electrode porosity and the internal surface of the pores is also important. For this last process, the use of a very thin coating on the electrode of an adsoption-dissociation catalyst, even as isolated islands, could markedly increase the sorption rate.

## Ohmic drops

Besides the electrode overpotentials two other sources of electrical energy losses raise some concern:

- Extra-ohmic drops in the electrolyte (segment **CB** in Fig.1) due to non-homogeneous current lines. Such a constriction of the current lines can, e.g., result from the electrode reaction occuring along the triple contact line only. 3-phase boundaries are doomed to be linked to an intrinsic inhomogeneity of the effective electrode active area.
- In-plane ohmic drops in the electrode between the current collecting spots. To ease this problems, the use of a second specific current-collecting layer on the top of the electrode could be considered. Whatever the selected solution, the *in-plane resistance* of the electrodes should always be measured.

## IV. Review and commentary on received contributions

## Gas diffusion in pores (see pages 9-20)

This well documented work by A. Solheim deals with the risk of diffusion energy losses (along the segment AC in Fig.1) at both the P and N electrodes. It shows that within easily acceptable limits, such energy losses can be maintained at a very low level, and converted into an electric parameter, this *voltage drop* has been set at 1 mV level.

Under the assumption of an electrode porosity in the range 20% to 40% and a pore tortuosity of about 2, the calculated limits are:

- Electrode thickness  $< 100 300 \ \mu m$ .
- Average pore diameter > 2  $\mu$ m.
- Current density  $< 2000 6000 \text{ A/m}^2$ .

The risk to overshoot the 1 mV loss level is slightly higher in almost pure or totally exhausted fuel, but such a situation will certainly not be encountered under regular operating conditions. Such a risk exists also when electrodes are coated on a thick porous substrate exceeding 1 mm.

The work has also been extended to the in-plane diffusion of the electroactive gases, underneath the current collecting spots. The loss varying with the square of the spot contact width, this should be smaller than 1 mm, if one wants to keep the loss under the 1 mV level.

The results of T. Saito (see p. 21-32) do confirm that there is no major limitation by gas diffusion in the pores.

Effect of the Ni and ZrO<sub>2</sub> morphologies on the negative composite electrode overpotential (see pages 21-32)

Two important conclusions can be drawn from the report of T. Saito, about technology and about modelling.

Measurements were mostly carried out with zirconia grains ranging from 0.5 to 40  $\mu$ m diameter and at various zirconia contents. The nickel grain size was maintained at 2.5  $\mu$ m (while attempts with smaller nickel grain were not successful).

The main conclusions are :

- The larger the nickel surface area in the electrode (i.e. the less agglomerated the nickel grains), the better the electrode.
- Small zirconia grains of 0.5 µm can prevent an agglomeration of the nickel grains during sintering (but not over a long operating time). With grains of this size, neither the zirconia content, nor the electrode porosity seem to be crucial parameters.

A comparison between the SANYO data and those of TOKYO GAS shows the similarity of the variation laws. The difference in magnitude of the optimum values can easily be explained by a larger nickel grain size, **d**, (which results in smaller ratio  $d_{ysz} / d_{NIO}$ !) and different sintering temperatures. This comparison would evidence a detrimental effect of a high sintering temperature (which can however be lowered with very fine YSZ powders).

About modelling, the results raise a question. Does the composite really act as a 3-dimensional electrode or is it only a microstructure capable of maintaining an appropriate morphology for the porous nickel in contact with the surface of the main electrolyte? The fact that the zirconia content does not play a major role (with gain size of  $0.5 \mu$ m) and that 10% of zirconia gives the best electrochemical results (though the largest obvious tailoring problem between the electrolyte and the anode layers), shows that *percolation* between the electronic grains on one hand and the ionic grains on the other is not essential (though it should be in a true 3-dimensional electrode). The magnitude of the current density also indicates that we are likely to be dealing with a regular 2-dimensional electrode. It would be interesting to see the influence of the electrode thickness.

## Morphological optimization of SOFC anode (see pages 33-42)

This work of N. Giordano et al. is an example of electrode modelling based only on readily available models in conventional electrochemistry:

- on a 3-dimensional electrode,
- the electrode reaction occurs on the free surface of the nickel grains (not at the triple contact line),
- there is a Tafel-Volmer determining electrode mechanism.

## Experimental determination of the kinetic rate data for SOFC anode (see pages 43-46)

The reported investigation of J. Parsons and S. Randall is just at its start. Succesful preliminary tests have ensured that a part of the experimental set-up performs satisfactorily.

## On the effective resistance of an electrolyte membrane (see pages 47-62)

Starting from a model set up by H. Tannenberger and H. Siegert back in the sixties, R. Herbin attempted to calculate the extra electrolyte resistance effect which results from non-homogeneous electrode reactions on the electrolyte surface (under the assumption that the electrode thickness is much larger than the distance between the electrode points of contact).

This mathematical approach is interesting in two ways:

- It provides a general method to solve similar problems.

It gives equations directly exploitable (at least for electrodes which do not deviate too much from an ideal grid model). The *coefficient of resistance*  $\alpha$  increases as the reciprocal of the electrode contact point number **n**:

$$\alpha = 1 + C/n$$

(where C is a constant equal to 3847), and roughly as the reciprocal of the electrode surface area, A:

$$\alpha = \mathbf{A}^{-\mathbf{k}}$$

(where k is a constant slightly smaller that 1).

The application of these formulas to practical SOFC situations has allowed to quantify the investigated effect, e.g., for

- an electrolyte thickness :10-4 m,
- a distance between electrode contact points : 10-5 m,
- an area of contact points : 10<sup>-14</sup> m<sup>2</sup>,

the coefficient of resistance  $\alpha = 1.22$ .

Coming from a different field, the access to the vocabulary is an important issue and a well defined list of symbols would be welcomed.

## Cathodic O2 reduction impedance at a known 3-phase boundary length (see page 63-65)

This is an interesting attempt by J. Van Herle to correlate an oxygen electrode reaction rate to the length of its triple contact line.

Gold was selected as an electrode material. The whole electrode surface was made sufficiently dense to impede any electrode reaction elsewhere than at the electrode periphery.

Unfortunately the experimental results revealed more complexity than expected (reading the report one could even conclude that nature is not willing to be modelled !). In fact, they demonstrate, among other things, the importance of the microcontainers of the electroactive species, in impedance spectroscopy. At equilibrium, oxygen adsorbed on the free electrolyte surface near the triple contact line and underneath the gold electrode has the same chemical activities.

What is the concentration underneath the gold electrode having the same chemical activity as adsorbed air outside? Certainly small, but not negligeable in terms of impedance measurements (as an indication, one can note that generally the electrode capacitance is related to the quantity of adsorbed oxygen and here, it does vary proportionally to the electrode surface).

## Oxygen stoichiometry and transport in SLM (see pages 67-72)

The very fine and systematic work of I.G. Krogh-Andersen et al. deals with the oxygen over-stoichiometry in LMN and the most common P electrode material  $La_{85}$  Sr<sub>.15</sub> Mn O<sub>3</sub>.

An original coulometric method has been developed. It deserves to be publicized, it seems convenient, accurate and suited to be applied to many other oxide systems.

The numerical results have been confirmed by thermogravimetric and chemical analysis. They all show that the investigated materials exhibit some oxygen excess under SOFC operating conditions.

They also confirm that the oxygen pressure range corresponding to the exact stoichiometry shifts toward higher oxygen pressure with the strontium doping.

It is claimed that from the thermogravimetric results one could calculate the oxygen diffusion coefficient in the materials, which is indeed an essential parameter for modelling the corresponding oxygen electrode reactions.

Berne, May 1992

Activity leader "Micromodelling"

Léo Dubal Head Fuel Cell R&D SWISS FEDERAL OFFICE OF ENERGY

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## 2. Gas Diffusion in Pores

A. Solheim (Norway)

## ABSTRACT

The diffusion coefficients for gases present in a solid oxide fuel cell were calculated from available equations. Expressions for the anodic and cathodic diffusion overvoltages are given. The overvoltages due to cross-plane diffusion through the electrodes were estimated to be in the order of 1 mV at the anode as well as the cathode for electrode thicknesses in the range 100-300 micron and current densities in the range 2000-6000 Am<sup>-2</sup>. Higher values would be expected for the anodic diffusion overvoltage near the fuel inlet in cells fuelled by pure hydrogen, however. A preliminary investigation indicates that the overvoltage due to inplane diffusion underneath the interconnector-electrode contact area in a flat plate cell is governed by the ratio between the square of the contact area width and the electrode thickness. By limiting the width of the contact area to less than 1 mm, the current density will not be substantially reduced at the center of the contact area.

### **1 DIFFUSION COEFFICIENTS**

### 1.1 Ordinary Binary Diffusion Coefficients (in Bulk)

The ordinary diffusion coefficient can be regarded as a physical constant for a binary mixture of gases. The diffusion coefficient varies approximately with  $T^{1.75}$ , and contrary to the other molecular transport coefficients (viscosity and thermal conductivity), it is inversely proportional to the total pressure, and it does not vary with the composition. The diffusion coefficient for binary mixtures can be estimated by the Fuller, Schettler, and Giddings equation /1/,

$$D_{12} = \frac{1 \cdot 10^{-7} \cdot T^{1.75} \cdot \left(\frac{1}{H_1} + \frac{1}{H_2}\right)^{\frac{1}{2}}}{P \cdot \left[ (\Sigma v_1)^{\frac{1}{3}} + (\Sigma v_2)^{\frac{1}{3}} \right]^2}$$
(1)

where  $D_{12}$  is the diffusion coefficient  $[m^2 \cdot s^{-1}]$ , T is the temperature [K], M is the molecular weight  $[g \cdot mol^{-1}]$ , P is the total pressure [atm], and  $\Sigma v$  is the "diffusion volume". The latter is an empirical constant which can be found in common textbooks /2,3/.

Alternatively, the diffusion coefficient can be estimated by the equation proposed by Hirschfelder, Bird, and Spotz /4/,

$$D_{12} = 1.858 \cdot 10^{-7} \cdot \frac{T^{\frac{3}{2}} \cdot \left(\frac{1}{M_1} + \frac{1}{M_2}\right)^{\frac{1}{2}}}{P \cdot \sigma_{12}^2 \cdot \Omega_D}$$
(2)

where  $\sigma_{12}$  and  $\Omega_{\rm D}$  are Lennard-Jones parametres, also available from common textbooks.

The AiChE Data Prediction Manual /5/ recommends Equation (1) in cases where values for the diffusion volumes can be found. Both equations above were derived under the assumption of non-polar molecules, and consequently errors may occur if one of the molecules is water or carbon monoxide.

The diffusion coefficient factor  $(D/T^{1.75})$  was calculated for binary systems of interest in solid oxide fuel cells, and the results are presented together with some literature data in Table I. As can be observed in the table, the numerical values clearly fall in two groups, depending on whether  $H_2$  is a part of the system or not. The agreement between measured and calculated data is generally good, with the possible exception of the system  $H_2O-CO_2$ . At low temperature, Equation (1) overestimates D with about 30 percent. None of the other systems containing  $H_2O$  or  $CO_2$  show such a high deviation. The high deviation in the  $H_2O-CO_2$  system can possibly be explained by association. If this is true, one would expect the error to decrease with increasing temperature.

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System	$\frac{D \cdot 10^{-9}}{T^{1.75}}$	T	$D_{T} \cdot 10^4 \ [m^2 \cdot s^{-1}]$		
			Measured	Calculated	Deviation [%]
0 <sub>2</sub> -N <sub>2</sub>	0.9692	273	0.181 <sup>a,b</sup>	0.178	-1.7
H <sub>2</sub> -H <sub>2</sub> O	4.107	273 293	0.75ª 0.85 <sup>b</sup>	0.753 0.852	(+0.4) (+0.2)
H <sub>2</sub> -CO	3.472	273	0.651 <sup>a,b</sup>	0.637	-2.2
H <sub>2</sub> -CO <sub>2</sub>	2.981	273 298	0.550 <sup>a,b</sup> 0.646 <sup>a</sup>	0.547 0.637	-0.5 -1.4
H <sub>2</sub> -CH <sub>4</sub>	3.216	273	0.625 <sup>a,b</sup>	0.590	-5.6
H <sub>2</sub> O-CO	1.209	273	2 <b>2</b> 11	0.222	
H <sub>2</sub> O - CO <sub>2</sub>	0.9847	273 298	0.138ª 0.164 <sup>b</sup>	0.181 0.210	+31 +28
H <sub>2</sub> O - CH <sub>4</sub>	1.253	273	<u>.</u>	0.230	
CO-CO <sub>2</sub>	0.755	273	0.137ª	0.138	+0.7
CO-CH4	1.011	273	-	0.186	-
CO <sub>2</sub> - CH <sub>4</sub>	0.8386	273	0.153 <sup>b</sup>	0.154	+0.7
0 <sub>2</sub> -H <sub>2</sub>	3.634	773	4.2ª	4.12	-0.9
0 <sub>2</sub> -H <sub>2</sub> O	1.235	723	1.3*	1.24	-4.6
0 <sub>2</sub> -C0	0.9515	723	1.0ª	0.959	-4.1
0 <sub>2</sub> -CO <sub>2</sub>	0.7550	773	0.9ª	0.856	-4.9
0 <sub>2</sub> -CH4	1.029	773	1.1ª	1.17	+6.4

<u>Table I</u>. Diffusion data at 1 atm total pressure for binary gas systems of interest in SOFC fuel cells. The diffusion coefficient was calculated from Equation (1).

<sup>a</sup> Data from Perry /6/ <sup>b</sup> Data from Welty, Wicks, and Wilson /2/

## 1.2 Knudsen Diffusion

If diffusion is taking place in small pores, the frequency of collisions between the diffusing molecule and the pore walls may eventually become more frequent than collisions with other gas molecules. In this case, the transport rate can be calculated using the Knudsen diffusion coefficient,

$$D_{1K} = \frac{d_p}{3} \cdot \left[ \frac{8 RT}{\pi M_1} \right]^{\frac{1}{2}}$$
(4)

where  $d_p$  is the pore diameter. Frequently, both ordinary diffusion and Knudsen diffusion are significant, in which case the diffusion coefficient can be estimated by

$$D_1 \approx \left[\frac{1}{D_{1K}} + \frac{1}{D_{12}}\right]^{-1}$$
(5)

Figure 1 gives some calculated diffusion coefficients for  $\rm H_2$  and  $\rm O_2$  in the binary systems  $\rm H_2-H_2O$  and  $\rm O_2-N_2,$  respectively, as a function of the pore diameter.

The transport rate through a porous plate is normally expressed in terms of the nominal thickness and surface area of the plate. The transport rate must therefore be corrected for the porosity  $\theta$ , defined as the ratio between pore volume and total volume, as well as the tortuosity factor  $\tau$ , which can be regarded as the ratio between the length of the real diffusion path and the plate thickness. The transport rate j can therefore be estimated as

$$j_1 \approx -\left[\frac{D_{12} \cdot D_{1K} \cdot \theta}{(D_{12} + D_{1K}) \cdot \tau}\right] \cdot \frac{P}{RT} \cdot \frac{dy_1}{dz} + j_{tot} \cdot y_1 \quad [mol \cdot m^{-2} \cdot s^{-1}]$$
(6)

where dy/dz is the gradient in molar fraction and  $j_{tot}$  is the total flux. Dealing with SOFC, the porosity of the electrodes would be expected to be in the range of 0.2 - 0.4 and the typical pore diameter in the order of 1 micron. The numerical value of the tortuosity factor  $\tau$  is often around 2. Hence, the "effective" diffusion coefficient in the porous phase (expression within brackets in Eq. (6)) would be expected to be about one order of magnitude lower than the bulk diffusion coefficient  $(D_{12})$ .

#### 1.3 Diffusion Coefficients in Mixtures of Multiple Components

In binary systems, the diffusion coefficient is independent of the composition. This is no longer valid if the mixture contains three or more components. The only way to estimate the diffusion coefficient is by the

simplified equation by Wilke /7/,

$$D_{i-Mix} \approx \frac{1-y_i}{\sum_{j \neq i} \frac{y_j}{D_{ij}}}$$

The standard deviation between Equation (7) and the very few measured data points available was found to be about 5 percent /5/.

In a plug flow methane fuelled SOFC with external reforming, the gas composition in the anode channel varies with the distance from the fuel inlet. Figure 2 gives the calculated diffusion coefficients for the components  $H_2$ ,  $H_2O$ , CO, and  $CO_2$  as a function of the degree of fuel utilization (based on the number of Faraday passed per mol  $CH_4$  in the feed to the reformer). The calculation was performed under the assumption of complete reforming (i.e., no  $CH_4$  left in the cell feed) and shift reaction in equilibrium at any point.

By calculating the molar fluxes, using the diffusion coefficients in Figure 2, an unexpected result appears.

Provided that no reactions proceed homogenously, and since the total molar flux is zero (equal number of molecules diffusing in either direction through a plane parallel to the electrolyte), the molar flux of each component in the mixture can be calculated as

$$j_i = -D_{i-Mix} \cdot \frac{P}{RT} \cdot \frac{dy_i}{dz}$$
(8)

H- and C balance gives

$$j_{\rm HO} = -j_{\rm H}$$
 and  $j_{\rm CO} = -j_{\rm CO}$  (9)

Assuming constant temperature and total pressure, Eqs. (8) and (9) combine to give

$$\frac{d y_{H_0}}{d y_{H_c}} = -\frac{D_{H_s}}{D_{H_0}} \quad \text{and} \quad \frac{d y_{CO_s}}{d y_{CO}} = -\frac{D_{CO}}{D_{CO_s}}$$
(10)

Since the sum of molar fractions is always unity, we must have

$$\sum_{i} dy_{i} = dy_{\mathbf{H}_{i}} \cdot \left[ 1 - \frac{D_{\mathbf{H}_{i}}}{D_{\mathbf{H}_{i}O}} \right] + dy_{\mathbf{CO}} \cdot \left[ 1 - \frac{D_{\mathbf{CO}}}{D_{\mathbf{CO}_{i}}} \right] = 0$$
(11)

Finally, from Eqs. (8) and (11) we calculate the ratio between the fluxes as

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(7)

$$\frac{\mathbf{j}_{\mathbf{H}_{i}}}{\mathbf{j}_{CO}} = \frac{\mathbf{j}_{\mathbf{H}_{i}O}}{\mathbf{j}_{CO_{i}}} = -\frac{\mathbf{D}_{\mathbf{H}_{i}} \cdot \left[1 - \frac{\mathbf{D}_{CO}}{\mathbf{D}_{CO_{i}}}\right]}{\mathbf{D}_{CO} \cdot \left[1 - \frac{\mathbf{D}_{\mathbf{H}_{i}}}{\mathbf{D}_{\mathbf{H}_{i}O}}\right]}$$

Since the diffusion coefficents for CO and  $H_2$  are always larger than the diffusion coefficients for  $CO_2$  and  $H_2O$ , respectively, the ratio between the fluxes must be negative. This implies that CO and  $H_2$  always would diffuse in opposite directions, as long as no homogenious reactions are taking place. At present, we have not analyzed how this would influence the modelling of processes taking place at the anode of a SOFC.

#### **2 DIFFUSION OVERVOLTAGE**

### 2.1 <u>Cross-plane Diffusion Overvoltage</u>

<u>Cathode</u>. By assuming the factor  $\theta/\tau$  to be 0.15 (e.g., porosity 0.3 and tortuosity factor 2) and typical pore diameters about 2 micron, the effective diffusion coefficient for oxygen becomes about  $2.5 \cdot 10^{-5} \text{ m}^2 \text{s}^{-1}$  at 1200 K. The molar flow of oxygen is

$$j = \frac{i}{4F}$$
(13)

where i is the current density  $[Am^{-2}]$  and F is the Faraday constant [96485 As equiv<sup>-1</sup>]. The diffusion overvoltage  $\eta$  becomes

$$\eta = \frac{RT}{4F} \ln\left(\frac{y^*}{y^0}\right) \tag{14}$$

where R is the universal gas constant  $[8.3145 \text{ Jmol}^{-1}\text{K}^{-1}]$  and y<sup>0</sup> and y<sup>\*</sup> are the molar fractions of oxygen at either side of the cathode. For cross-plane diffusion, Eqs. (6), (13), and (14) can be combined to give

$$\eta = \frac{RT}{4F} \ln \left\{ \frac{1}{y^0} - \left(\frac{1}{y^0} - 1\right) \cdot \exp\left[\frac{iRTt}{4FD_{eff}P}\right] \right\}$$
(15)

where t is the thickness of the cathode. Figure 3 shows the cathodic overvoltage as a function of the current density for different cathode thicknesses. As can be observed, the cathodic diffusion overvoltage would be small in most situations. For a cathode thickness of 200 micron the

(12)

overvoltage becomes -0.86 mV at 4000 Am<sup>-2</sup>. It follows from Eq. (15) and Figure 3, however, that the cathodic overvoltage may be significant if the cathode is located on a porous support.

Anode. It follows from Figure 1 that the effective diffusion coefficient at the anode in a hydrogen fuelled cell is about 4-5 times larger than at the cathode, provided that the morphologies of the anode and the cathode are comparable. In addition, the anode would normally be thinner than the cathode. This indicates that the anodic diffusion overvoltage would be small compared to the cathodic overvoltage. On the other hand, the molar flow densities of hydrogen and water equals i/2F rather than i/4F as in Eq. (13), and the overvoltage depends on the molar fractions of both water and hydrogen. The anodic diffusion overvoltage becomes

$$\eta_{a} = \frac{RT}{2F} \ln \left( \frac{y_{H_{a}}^{0} \cdot y_{H_{a}}^{*}}{y_{H_{a}}^{0} \cdot y_{H_{a}}^{0}} \right)$$
(16)

On the anode side of a hydrogen fuelled cell the overall molar flow is zero. and the difference between the molar fractions at either side of the anode becomes ("\*" denotes the electrolyte/anode interface)

$$y_i^* - y_i^0 = \pm \frac{iRTt}{2FD_{eff}P}$$
(17)

where the "+" sign applies for water and the "-" sign for hydrogen. Hence, the anodic diffusion overvoltage becomes

$$\eta_{a} = \frac{RT}{2F} \cdot \ln \left( \frac{1 + \frac{iRTt}{2FD_{off}Py_{H_{i}}^{0}}}{1 - \frac{iRTt}{2FD_{off}Py_{H_{i}}^{0}}} \right)$$

By inserting the following numerical values in Eq. (18):  $i = 5000 \text{ Am}^{-2}$ , T = 1200 K,  $D_{eff} = 1 \cdot 10^{-4} \text{ m}^2 \text{s}^{-1}$ ,  $P = 1.013 \cdot 10^5 \text{ Pa}$ , and t = 100 micron, we calculate  $\eta_a = 0.53$  mV for equal molar fractions of water and hydrogen. The overvoltage is considerably higher near the fuel inlet however, as shown in Figure 4. A similar increase in the diffusion overvoltage would be observed near the exhaust end of the fuel channel at very high fuel utilization. This will probably not be a problem in practice, since the current density is going to be low in that region, and since the fuel utilization is limited due to passivation of the nickel cermet anode at a too high water/hydrogen ratio.

A rigorous modelling of the anodic diffusion overvoltage in reformed methane fuelled cells is not possible at the moment.

(18)

### 2.2 In-plane Diffusion Overvoltage

In flat plate fuel cell designs, the non-porous interconnector is supplied with ribs in order to form channels for the transport of fuel and oxygen. The ribs are brought in contact with the electrodes to provide current contact. This design gives in-plane diffusion of gases through the porous electrode underneath the interconnector/electrode contact area, as well as the normal cross-plane diffusion. It is important that the ribs on the interconnector are not too wide, or cover a too large fraction of the total electrode area, since this would impede the transport of gases to the reaction zone.

A preliminary treatment indicates that the ratio between the diffusion overvoltage underneath the interconnector ribs and the overvoltage due to pure crossplane diffusion is governed by the ratio between the square of the rib width  $(W_r)$  and the thickness of the electrode. The overvoltage at the center of the rib will be limited to about five times the crossplane diffusion overvoltage if

 $\frac{W_r^2}{t} < \approx 0.008 \text{ m}$ 

(19)

This corresponds to a rib width of about 0.9 mm for an electrode thickness of 100 micron. By limiting the overvoltage to about five times the crossplane overvoltage, the current density underneath the interconnector rib will not be substantially influenced in normal situations. Special problems may occur near the fuel inlet, however, as indicated above.

A more detailed study considering the inplane diffusion is in progress.

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Figure 1. Binary diffusion coefficients for hydrogen and oxygen in the systems  $H_2/H_2O$  and  $O_2/N_2$ , respectively, as a function of the pore diameter at different temperatures.



Degree of fuel utilization

Figure 2. Bulk diffusion coefficients for components on the anode side of an externally reformed SOFC at 1200 K. Parameter:  $H_2O/CH_4$  molar ratio in the feed to the reformer. It was assumed that the reforming is complete (no CH<sub>4</sub> left in the cell feed) and that the shift reaction is in equilibrium at any point.



Figure 3. Cathodic diffusion overvoltage as a function of the current density at different cathode thicknesses [microns] as indicated in the figure. T = 1200 K,  $y^0 = 0.2$ ,  $D_{eff} = 2.5 \cdot 10^{-5} m^2 s^{-1}$ , and P = 1.013  $\cdot 10^5$  Pa.



Figure 4. Anodic diffusion overvoltage in a hydrogen fuelled cell as a function of the molar fraction of hydrogen. Parameter: Current density  $[Am^{-2}]$ . T = 1200 K,  $D_{eff} = 1.0 \cdot 10^{-4} m^2 s^{-1}$ , P = 1.013 $\cdot 10^5$  Pa, and anode thickness t = 100 microns.

## 3. Effect of Ni and ZrO<sub>2</sub> on Anode Performance

## T. Saito (Japan)

## 1. Introduction

The design requirements for SOFC electrodes which are operated at high temperatures are:

- 1. An active place for the gas reaction
  - · Proper three phase boundary
- · Sufficient diffusion of fuel, oxidant and reaction product.
- 2. Excellent contact between electrode/electrolyte
- ·Maintained contact between solid state materials
- 3. Long-term stability of electrodes and electrolyte • Prevention of sub-reactions between components

Therefore we introduced the concept of the "composite electrode" as an electrode structure that satisfies these requirements.

The "composite electrode" basically consists of an ideal combination of electrodes and electrolyte, which meets the above-mentioned demands.

In order to achieve this objective, we paid particular attention to the anode, which consists of Ni electrode materials and YSZ electrolyte materials. We determined a suitable mixture ratio by varying the particle sizes and contents, and by examining the influence of surface area and porosity on anode performance.

2. Experimental

Materials

Table 1 shows the materials and thickness for each component of the test cells.

Metal nickel powders of known particle size and surface area were used as the anode Ni materials.

# Cell constructionAnode slurry was prepared by mixing different ratios<br/>of Ni and YSZ powders in Terpineol. The slurry was<br/>painted on to a commercial YSZ plate and dried.<br/>Platinum mesh was covered to form an electrical<br/>collector, and electrical leads were attached.<br/>The cell was set at the center of the divided $Al_2O_3$ <br/>tube with glass seal (Fig. 1).

The reference electrode (same material as the cathode) was positioned on the cathode side.

## Evaluation

Volume change of electrode: Volume change of anode was measured as shown in Fig. 2.

Electrochemical evaluation: Various polarization factors (electrolyte resistance, contact resistance, anodic polarization and cathodic polarization) were divided by AC impedance and current interruption methods, and were evaluated in detail, including the usual I-V measurements. (Table 1).

Evaluation of physical characteristics: Ni surface area in electrodes was measured by the BET method and porosity was analyzed by porosimeter.

## 3. Results & Discussion

(1) Mixture ratio

We selected four kinds of YSZ powder with particle diameters 0.5, 5, 10, and 40  $\mu$  m. The YSZ content of the samples were 10~70 wt%. We measured their volume change and the interface resistance of the anode.

Regarding the volume change, when the YSZ content was 50 wt% or more, no change was observed after 5 hours, as shown in Fig. 3. But at YSZ contents of less than 50 wt%, a gradual change was observed.

Thus, we deduce that 0.5  $\mu$  m YSZ was suitable for maintaining electrode structure and electrical conductivity.

(2) Cell performance and surface area

Next, the cell's performance was evaluated practically, Cell voltage was analyzed at a constant current density of 300 mA/cm<sup>2</sup> and interface resistance was measured by the AC impedance method.

The results are shown in Figs. 4 and 5. These results indicate that optimum cell performance was obtained with 0.5  $\mu$  m YSZ.

In order to clarify the dependence of optimum performance on YSZ content, we observed the micro-structure of the electrodes by SEM and EPMA. 0.5 and 40  $\mu$  m samples having 10 wt% YSZ contents were used to evaluate the remarkable difference in cell performance.

The results are shown in Figs. 6 and 7. From these SEM photographs, rapid sintering of Ni particles was observed in the electrode containing 10 wt%  $40\,\mu$  m YSZ. In 0.5  $\mu$  m YSZ, however, the Ni is barely sintered after 5 hours at 1000°C, and it retains the pores which are necessary for gas diffusion.

It is probable that the surface area of the electrode changes as a result of this sintering, so we measured the surface area of the electrode by the BET method.

Fig. 8 shows the relationship between the measured surface area of an electrode containing 50 wt% YSZ and the interface resistance of the anode shown in Fig. 5. There is a clear correlation between interface resistance and the surface area of the electrode.

We also examined the relationship between the interface resistance and surface area for other kinds of Ni particle. Ni surface area was calculated by separately measuring the surface area of the electrode itself and that of the YSZ particles.

In this experiment the Ni particle sizes were 1, 2.5, 5, and 8  $\mu$  m, and the YSZ particle size was 0.5  $\mu$  m and its content 10 wt%.

The results in Fig. 9. show a similar relationship between the Ni surface area in the electrode and the interface resistance, to that shown in Fig. 8.

Considering these results, We presume that the number of reaction points is related to the Ni surface area, and it is therefore possible to improve the anode efficiency by optimizing Ni and YSZ.

- (3) Cell performance and porosity
  - Next, we selected porosity from among the various electrode characteristics and studied its effect on anode efficiency. We prepared anodes with porosity values ranging from 65 to 85% by changing the composition of the slurry, and examined the relationship between porosity and the interface resistance of the anode. The results are shown in Fig. 10. The interface resistance was unaffected over this porosity range and remained almost constant, although there was slight variation in cell performance

To measure the effect of time on porosity, an electrode sample with an initial porosity of 65% was kept at 1000°C for 100 hours. Although the interface resistance changed during cell operation, the porosity remained almost constant as shown in Fig. 11.

This confirmed that the anode interface resistance is mainly affected by the Ni surface area, but barely affected by porosity over this range.

## 4. Conclusions

We examined SOFC anode performance using various Ni and YSZ particles. As a result, we determined that:

- It is possible to improve the anode performance by optimizing the Ni and YSZ particle sizes and their weight ratios.
- (2) The interface resistance of the anode is mainly determined by the Ni surface area; cell performance improves with increasing Ni surface area.
- (3) The interface resistance of the anode is not affected by its porosity, over a range of about 65-85%.

## Acknowledgement

This work was supported by NEDO, under the Moon Light Project of the MITI.

<Experimental>

• Test Cell

Active area		0.5cm²		
	Anode	Ni(NiO)/YSZ, 100;m		
Material	Cathode	La <sub>o.9</sub> Sr <sub>o.1</sub> MnO <sub>3</sub> /(YSZ), 100µm		
	Electrolyte	PSZ, (YSZ), 200≢m		
	Reference	La <sub>o.9</sub> Sr <sub>o.1</sub> MnO <sub>3</sub> /(YSZ), 100µm		
Gar	Fuel	H <sub>2</sub> +3%H <sub>2</sub> 0		
Gas	Oxidant	O2(Air)		
Temp.		1000r		
Standard density	current	300mA/cm²		

· AC impedance measurement



Time (# · sec)

# Table.1 Materials and thickness of components









Fig.3 The relationship between YSZ content and volume change with various particle size of YSZ



Fig.4 The relationship between YSZ content and cell voltage with various particle size of YSZ



Fig.5 The relationship between YSZ content and interface resistance with various particle size of YSZ



Fig.6 SEM Photograph of Ni-YSZ surface



**YSZ 0.5**µm



YSZ 40µm

2µ....

Temperature	1000 <sup>°</sup> C	
Time	5 hrs	
YSZ Content	50 wt%	
Diameter of Ni particle	2.5//m	

## Fig.7 Distribution of Ni and YSZ in Anode







Fig.9 The relationship between surface area of Ni and interface resistance of anode



Fig.10 The relationship between porosity and interface resistance of anode



Fig.11 Change of porosity and interface resistance on anode

## Comments

Fig. 1 shows the comparision of both Tokyo Gas and Sanyo data from the viewpoint of the overpotential against d(YSZ)/d(NiO). The overpotential had the minimum value between d(YSZ)/d(NiO) of  $10^{-2}$  and  $10^{-1}$  in Tokyo Gas data. On the other hand, our data had that between  $10^{-1}$  and  $10^{0}$ .

Fig. 2 or 3 show the relationship between the overpotential and YSZ or Ni(NiO) particle size from fig.1. In fig.2 the overpotentials decreased with decrease of YSZ particle size in both Tokyo Gas and Sanyo data and it also decreased with decrease of sintering temperature.

In fig. 3, the overpotential increased with increase of Ni particle size which related to the Ni surface area. I cannot exactly explain the phenomina at A region, but some anode sintering seemed to occur and reduce the active surface area unexpectedly.





() VSZ 0.5#m 10wt%---Ni 1#m,2.5#m,4#m,8#m

- 2 A . Ni 2.5#m 90wLZ-- YSZ 40#m.10#m.5#m.0.5#m
- ③ □ NIO 1.0## 56wt% --YSZ 10##.0.5##



Fig. 3

## 4. Morphological Optimization of a SOFC Anode

G. Maggio, I. Ielo, V. Antonucci & N. Giordano (Italy)

## GOALS

- 1) To determine the role of morphological variables (support surface area, porosity, average pore radius) on the anode reaction in a SOFC.
- 2) To identify an optimal morphological configuration of the electrode structure.

For these purposes it has been used a theoretical approach (MODELLING), determining the results on the basis of analysis in terms of limiting current.
## SYSTEM AND OPERATING CONDITIONS

The model here presented is of the "micro-level" type.

The reference system is:

Ni-ZrO<sub>2</sub> Anode Fuel 100% H<sub>2</sub> P=1 atm T=1273°K 40 v/o Ni

SCHEMATIC VIEW OF Ni-ZrO<sub>2</sub> ANODE



ELECTROLYTE YSZ

## **GENERAL ELECTRODIC PROCESSES**

The electrodic reaction in a porous electrode evolves according to the following sequence:

- a) Diffusion of reactants from the fluid phase to the external catalyst surface
- b) Diffusion of reactants from the external to the internal catalyst surface
- c) Adsorption of reactants
- d) Surface reaction on catalyst
- e) Desorption of products
- f) Diffusion of products from the internal to the external catalyst surface
- g) Diffusion of products from the external catalyst surface to the fluid phase.

In the SOFC's operating conditions (see previous page) the external diffusion effects (a and g steps) are negligible (high temperature); besides, the effects of conduction should not constitute a controlling step (40v/o Ni) and thus the result is a competition between kinetics (c,d and e) and internal diffusion (b and f).

## **MODEL EQUATIONS**

To evaluate the contribution by the diffusive and kinetic terms, the following equations have been adopted:

$$2 \cdot F \cdot D_{ef} \cdot \frac{d^2 C_{H2}}{dx^2} = A \cdot j \qquad [1]$$

$$C_{H2} = C_{H2}^{\circ} AT x=0$$
  
 $dC_{H2}/dx = 0 AT x=L$ 
[1A]

$$j = j_0 \cdot \left[ \frac{1}{\theta_0 + (1 - \theta_0) \cdot e^F \eta / RT} \right]^2 \cdot \left[ \frac{C_{H_2}}{C_{H_2}} \cdot e^{2F \eta / RT} - 1 \right] [2]$$

$$j = -2 \cdot F \cdot D_{ef} \cdot (dC_{H_2}/dx)_{x=0}$$
 [3]

Eq. 1: Steady-state diffusion at a planar porous electrode

Eq. 1A: Boundary conditions

- Eq. 2: I-V Relationship
- Eq. 3: Fick's law of diffusion

where:

 $\begin{array}{l} D_{ef}: effective \ diffusion \ coefficient \\ C_{H_2}: \ hydrogen \ concentration \\ A \quad : \ cm^2 \ active \ Ni/cm^3 \ of \ layer \\ j_o: \ exchange \ current \ density \\ \Theta_o: \ surface \ coverage \ by \ hydrogen \ at \ equilibrium \end{array}$ 

In particular, eq.[2] was derived assuming that the anodic *E* oxidation reaction proceeds according to the Tafel - Volmer sequence, with the dissociation reaction (Tafel) as RDS.

## DETERMINATION OF THE LIMITING CURRENT

Solving the system of differential equations [1]-[1A]-[2], the eq.[3] for current density becomes:

$$j = 2 \cdot F \cdot D_{ef} \cdot C^{\circ}_{H2} \cdot \sqrt{\sigma} \cdot (1 - e^{2F \eta / RT}) \cdot \tanh(L\sqrt{\sigma})$$
[4]

where

$$\sigma = \frac{A \cdot j_{o}}{2 \cdot F \cdot D_{ef} \cdot C^{\circ}_{H_{2}}} \cdot \left[\frac{e^{F \eta / RT}}{\theta_{o} + (1 - \theta_{o}) \cdot e^{F \eta } / RT}\right]^{2} \quad [5]$$

$$j_0 = 2 \cdot F \cdot k \cdot C^{\circ}_{H_2} \cdot (1 - \theta_0)^2 \qquad [6]$$

k: Rate constant for molecular dissociation of hydrogen.

For  $l\sqrt{\sigma} > 1$  (very fast reaction; i.e. high  $j_0$ , likely expected at the high SOFC's temperatures) eq. [4] reduces to

$$j = 2 \cdot F \cdot D_{ef} \cdot C^{\circ}_{H2} \cdot \sqrt{\sigma} \cdot (1 - e^{2F} \eta / RT)$$

when  $\eta \longrightarrow \infty$  the limiting current  $j_{lim}$  is obtained:

$$j_{\lim} = 2 \cdot F \cdot C^{\circ}_{H2} \cdot (A \cdot k \cdot D_{ef})^{1/2}$$
<sup>[7]</sup>

This equation expresses the limiting current as a function of the kinetic (k) and the diffusive  $(d_{ef})$  term.

## **DERIVATION OF PARAMETERS**

The role of average pore radius  $\overline{r}$ , is implicit both in the morphological term A (determined on the basis of simple geometric considerations) and in the diffusive term  $d_{ef}$  (determined by the combination of the Knudsen diffusion and self-diffusion):

$$A = \frac{C_1 \cdot r_{Ni}}{2C_3 + C_1 \cdot \overline{r}}$$

Active surface of Ni

 $D_{ef} = \frac{c_4 \cdot \bar{r}}{c_5 \cdot \bar{r} + D_B} \frac{c_1 \cdot \bar{r}}{2c_3 + c_1 \cdot \bar{r}} \frac{1}{\tau}$  Effective diffusion

where

$$C_{1} = SA \cdot {}^{\varrho}Ni \cdot {}^{\varrho}ZrO_{2}$$

$$C_{2} = 2 \cdot C_{1} \cdot {}^{\varrho}ZrO_{2} + (1 - f_{Ni}) \cdot {}^{\varrho}Ni$$

$$C_{4} = D_{B} \cdot C_{5}$$

$$C_{5} = 9700 \cdot \sqrt{(T/M)}.$$

A relationship between the catalyst layer porosity  $\Theta$  and r was also derived:

$$\Theta = \frac{c_1 \cdot \overline{r}}{2c_3 + c_1 \cdot \overline{r}}.$$

## LIMITING CURRENT BEHAVIOR

Substituting the values of the parameters A and  $d_{ef}$  in eq. [7], we obtain  $j_{lim}$  as a function of  $\bar{r}$ 

$$j_{\lim} = 2 \cdot \mathbf{F} \cdot \mathbf{C}^{\circ}_{H2} \cdot \left[ \frac{\mathbf{C}_{1} \cdot \mathbf{C}_{2} \cdot \mathbf{C}_{4} \cdot \mathbf{k} \cdot \mathbf{f}_{Ni} \cdot \overline{\mathbf{r}}^{2}}{\tau \cdot (\mathbf{C}_{5} \cdot \overline{\mathbf{r}} + \mathbf{D}_{B}) \cdot (2\mathbf{C}_{3} + \mathbf{C}_{1} \cdot \overline{\mathbf{r}})^{2}} \right]^{1/2}$$
[8]

The derivative (dj<sub>lim</sub> /dr) allow to determine the optimal average pore radius

$$\bar{r}_{opt} = c_3/c_1 + [c_3/c_1 \cdot (c_3/c_1 + 4 \cdot D_B/c_5)]^{1/2}$$
[9].

The following table summarizes the optimal  $\bar{r}$  values deduced from eq.[9], for various SA (surface area of the ZrO<sub>2</sub> porous support) and  $f_{Ni}$  (Ni weight percentage in catalyst layer):

f <sub>Ni</sub> ·100 (w/o)	SA $(m^2/g)$	r <sub>opt</sub> (μm)
3.0	0.05	7 20
30	0.5	1.25
30	5.0	0.32
50	0.05	6.79
50	0.1	3.82
50	0.5	1.19
50	1.0	0.77
50	5.0	0.30
50	10.0	0.21
70	0.05	6.30
70	0.5	1.13
70	5.0	0.29

The results are reported in terms of the behavior of  $j_{lim}$  as a function of average pore radius considering:

- 1) Fixed  $f_{Ni}$  (50w/o Ni) and different surface areas (from 0.05 to 10 m<sup>2</sup>/g)
- 2) Fixed surface area (SA = 0.5 and  $5.0 \text{ m}^2/\text{g}$ ) and different Ni percentages (from 30 to 70w/o Ni).

The values of  $j_{lim}$  were determined in arbitrary units from an equivalent form of eq. [8].; the effective values can be explicitly obtained from eq.[8], as  $c_{H_{\gamma}}^{\circ}$  and k are known.

# J<sub>lim</sub> BEHAVIOR AS A FUNCTION OF AVERAGE PORE RADIUS AT DIFFERENT SURFACE AREAS.



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# J<sub>lim</sub> BEHAVIOR AS A FUNCTION OF AVERAGE PORE RADIUS AT DIFFERENT Ni-PERCENTAGES.



ator Manager Institute

## CONCLUSIONS

From this analysis we can conclude that:

- 1) The role of some morphological variables is critical on limiting current of sofc anode. In particular:
  - a) j<sub>lim</sub> increases when the support surface area decrease
  - b) j<sub>lim</sub> increases as the Ni percentage increases, for given surface area (this treatment leave conducibility problems out of consideration).
- 2) A morphological optimization results from the choice of a particular value of average pore radius (or catalyst porosity). In particular:
  - a) at lower surface areas (SA < 0.1 m<sup>2</sup>/g) the limiting current density is almost independent from the average pore radius, its maximum being located at around 4-7 $\mu$ m
  - b) at higher surface areas the influence of  $\overline{r}$  is more drastic and the maximum limiting current is localized in a narrow range of average pore radius (0.2-1.2µm)
  - c) the optimal average pore radius is not significantly affected by Ni percentage.

### 5. Experimental Determination of Kinetic Rate Data for SOFC Anodes

#### J. Parsons & S. Randall (United Kingdom)

The Watson House Research Station of British Gas plc is collaborating with SI, Oslo, in experimentally determining kinetic rate data for a variety of anode materials. To this end SI have plasma sprayed a range of metal supports with nickel cermets and supplied them to Watson House.

A SOFC test facility has been built at Watson House in order study the operation of 5cmx5cm single cells. It was intended to use this to characterise the reforming activity of these plates. However, at present the single cells are sealed to a 'macor' fuel manifold block using a glass cement. Due to the difference in thermal expansion coefficient between the macor block and the metal support block it is not possible to use a glass cement for sealing. A new fuel manifold design and sealing method, using a gold gasket, is in the process of being designed, Fig. 1. We anticipate that the design will be finalised by the end of July and the re-build completed during September. As soon as the revised facility is ready the SI plates will be characterised.

Although no experimental work has been carried out on the SI plates yet, we have conducted a similar experiment on a cell anode. This work is described in this report as the technique and analysis used are the same as will be used for the SI plates and because the results are of interest in their own right.

The cell used was provided by Imperial College and was based on an extruded 3YSZ foil, 250 $\mu$ m thick. The anode was a 40 $\mu$ m thick, nickel cerment, 40% nickel by volume, tape cast onto the foil. Its active area was 41mmx41mm. The cermet was made up with nickel oxide powder and sintered in air. The cell was sealed to the fuel manifold with a glass cement. It was then heated to 960°C in air. Once at temperature the fuel stream was flushed with nitrogen before being reduced with hydrogen. After the cell performance had been measured with a 2/1 H<sub>2</sub>/N<sub>2</sub> supply the N<sub>2</sub> was turned off and water was added to the H<sub>2</sub> supply, initially at 2.5% and rising to 75%. During this period the cell was kept open circuit and the cell voltage monitored. The voltage was plotted against the steam composition and this curve is shown in Fig. 2 with the calculated Nernst potential for the steam/H<sub>2</sub> mixture. The close fit between the two curves suggests good sealing of the cell and good control of the steam fraction.

Having reached  $3/1 H_2O/H_2$  mole ratio the  $H_2$  was turned off and the CH<sub>4</sub> supply turned on at the same mole ratio. A series of tests were then performed, supplying varying total flow rates of  $H_2O/CH_4$  and analysing the gas leaving the anode on a gc. This was repeated with the cell producing 0.04A (Run 1) and open circuit (Run 2). Once these test were completed the fuel was returned to  $H_2/N_2$  and then the fuel stream was purged with  $N_2$  before that too was turned off. The anode was left overnight in air at 960°C and the next day the above procedure was exactly repeated (Runs 3 and 4).

The results were fitted to an equation of the form:

```
\frac{dn_{CH4}}{dt}
```

where:

```
n = quantity of CH4 [mol]
t = time [s]
k = reaction rate constant [mol.s<sup>-1</sup>.atm<sup>-1.25</sup>]
P(CH4) = partial pressure of CH4 [atm]
```

The reaction rate constant k is defined in terms of the whole plate. At 960°C the following values were calculated for k as defined in the above equation:

 $= k P(CH_4)^{1.25}$ 

Run	and Silver K repaired and t
1	1.7x10 <sup>-3</sup>
2	$2.0 \times 10^{-3}$
3	$2.2 \times 10^{-3}$
4	$2.4 \times 10^{-3}$

The shift reaction is difficult to extract from the data but it was found that the data was best represented by relating the actual composition to the equilibrium constant:

 $\frac{P(CO_2) P(H_2)}{P(CO) P(H_2O)} = 0.65 \text{ Kp}$ 

where:

P(xx) is the partial pressure of xx

Kp is the equilibrium constant for the shift reaction at 960°C

As these results are only from one cell it would not be safe to draw broad conclusions for nickel cermet anodes from them. Measurement of the cell performance throughout the tests showed a steady decline. This was partly restored when the anode was oxidised and re-reduced. It is believed that the loss of performance was due to increasing anode resistivity. Due to this, and the low oxygen flux resulting from the cell connection arrangement it is not possible to make any positive comment on the effect of cell operation on reforming activity.

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# 6. On the Effective Resistance of an Electrolytic Membrane

#### R. Herbin (Switzerland)

#### Abstract

This work is concerned with the determination of the effective resistance of the electrolyte of a solid oxide fuel cell. Experimentally, the electrode/electrolyte interfaces of a cell has proven to be conductive at discrete spots only. In order to help the understanding of the electrochemical mechanism of this phenomenon, we study here the variation of the effective resistance of the electrolyte with respect to some of the parameters defining the geometry of the active regions of the interface. The major difficulty of the problem is the possibly great number of small active regions. An asymptotic study is carried out, which shows the behaviour of the resistance as the number of active regions grows. This analysis is useful for the determination of accurate numerical solutions.

#### 1. Introduction

The aim of this study is to compute the effective resistance of the electrolytic membrane of a solid oxide fuel cell (SOFC). SOFC's exist at an experimental state only, and little has been done in mathematical modeling. Because of the complexity of SOFC's, several levels of modeling can be considered (see e.g. (Selman, 1989)). Here, we are concerned with one aspect of "micromodeling", i.e. the mathematical model of the electrolyte/electrode interface.

In the next section, we shortly describe the principle of a SOFC, and we present the physical problem which is to be solved in order to determine the effective resistance of the electrolytic membrane of a SOFC. In Section 3, the mathematical model and the parameters which define it are presented. One of these parameters is the number of contact areas on the electrode/electrolyte interface; in Section 4, an asymptotic study of the behaviour of the effective resistance is performed as the number of contacts goes to infinity. This asymptotic study will be of great importance to check the accuracy of the numerical results, which are presented in the last section.

#### 2. Description of the physical problem

The principle of an oxide fuel cell is the direct conversion of chemical energy into electricity and heat. The reactive components of the cells are separated by an electrolytic membrane ; this membrane is made out of a solid oxide, which is pervious to ions but impervious to neutral molecules or atoms. The electrolyte is located between two porous electrodes. The air oxygen goes to the electrolyte through the positive electrode (cathode) ; at the interface electrode/pores/electrolyte, the oxygen molecules are ionised, each atom absorbing two electrons of the cathode (which is linked to the conductive part of the cell). On the other side of the electrolyte, these ions give two electrons which are conducted by the anode, and the oxygen reacts with the fuel (methane, for instance) and gives reaction products.

One important parameter for the efficiency of the cell is the electrolyte resistance which is minimised by using very thin electrolyte membranes. However, it has been found experimentally that the part of the internal resistance of a solid oxide fuel cell which is associated with the current flow through the solid oxide membrane is higher than the value given by the resistance of the solid oxide crossed by a homogeneous electric current. One possible reason for this fact is that the current flow through the oxide membrane is not homogeneous. Indeed, An electrochemical model (Tannenberger-Siegert,1969) was set up on the assumption that the current penetrates and leaves the electrolyte membrane at discrete spots only, hence the assumption of "active regions" which can be viewed as contact areas.

In order to interpret experimental results on SOFC elements and to optimise the electrodes configuration, it is important to have a quantitative relation between the increase of the ohmic loss and the relevant geometric parameters which define the contact areas. A convenient expression to describe this resistance increase is the ratio  $\alpha = R_{eff}/R_0$ , where  $R_{eff}$  is the effective resistance of the electrolyte membrane due to the nonhomogeneous current distribution, and  $R_0$  is the resistance of the membrane crossed by a homogeneous current flow :  $R_0 = \rho d/S$ , where  $\rho$  is the resistivity of the material, d the thickness of the membrane and S the area of the membrane under consideration. Mathematically, the calculation of  $R_{eff}$ requires solving the Laplace equation for given boundary conditions.

#### 3. The mathematical problem

We consider the domain  $\Omega(L,H) = ]0,L[x]0,L[x]0,H[$  depicted on Figure 1, which represents half of the electrolytic membrane, made out of a homogeneous material of resistivity  $\rho$ . The upper plane of the domain is the electrode/electrolyte interface, which is divided into n x n small squares which are all translated from an elementary square [0,b]x[0,b] on which a contact area is assumed to be symmetrical with respect to the axes x = -b/2, y = -b/2, and of area  $a^2$ , such that  $n^2 a^2 = A^2$  ( $A^2$  is therefore the total contact area. We assume that the contact areas are symmetrical with respect to the x and y axes, and we denote by C(L,n,A) the total contact area. On this contact area, a potential U<sub>1</sub> is imposed. Since the non-shaded area of the upper plane is non-conductive, grad u. n = 0 holds there. The bottom plane, denoted by S(L), represents the middle plane of the electrolytic membrane, where the electric current is assumed homogeneous (in fact, electrochemical evidence suggests that the homogeneisation of the electric current takes place very close to the upper surface). Hence a potential U<sub>0</sub> is imposed on the whole plane (x,z) at y~= 0.





The domain depicted on Figure 1 represents a part only of the electrolyte membrane itself, and periodical boundary conditions are assumed on all vertical sides of the domain (i.e. at x = 0, x = L, y = 0 and y = L).

Since the solid oxide is homogeneous, the resistance of the volume  $\Omega(L,H)$  crossed by a homogeneous electric current is  $R_o = \frac{\rho}{L^2}$ . Our purpose here is to compute the effective resistance of the material when the contacts are as shown on Figure 1. More specifically, we want to know the increase of resistance that we have compared to the situation where the area of contact is the whole of the upper plate; to this purpose, we compute the coefficient  $\alpha = \frac{R_{eff}}{R_o}$  (>1) where  $R_{eff}$  is the effective resistance, i.e. the ratio of the potential difference between the contacts and the bottom plane by the electrical flux on the bottom plane.

Since the resistivity  $\rho$  is homogeneous, constant througout the domain, we can consider it to be 1. The electrical current is thus  $\mathbf{j} = -\mathbf{grad} \mathbf{u}$ , and since div  $\mathbf{j} = 0$ , we have  $\Delta \mathbf{u} = 0$  in  $\Omega(\mathbf{L}, \mathbf{H})$ .

The problem to be solved in a convenient sense is thus :

	grad u. n = 0 on $\partial \Omega(L,H) \setminus (C(L,n,A) \cup S(L))$
	$u \equiv 0$ on S(L),
(1)	$u \equiv 1$ on C(L,n,A),
	$-\Delta u = 0$ in $\Omega(L,H)$ ,

where **n** denotes the outward normal to the boundary  $\partial \Omega(L,H)$ . Let E(u) be the energy associated with this problem; we introduce the variational formulation of problem (1) by minimising the energy over the set of admissible functions, i.e. we want to :

(2) Find  $u \in K(L,H,n,A)$  such that  $E(u) \le E(v) \forall v \in K(L,H,n,A)$ ,

where  $K(L,H,n,A) = \{v \in H^1(\Omega(L,H)); v \equiv 0 \text{ on } S(L), \text{ and } v \equiv 1 \text{ on } C(L,n,A)\}$ , and E(u) is the energy related to the problem, i.e.:

$$E(u) = \int_{\Omega(L,H)} ||grad u||^2 \, dx \, dy \, dz,$$

where ||.|| denotes the Euclidean norm on IR<sup>3</sup>. It is well known that problem (2) has a unique solution (see e.g. (Daultray-Lions(1987)). Note that, formally,  $E(u) = \int_{\partial \Omega(L,H)} u \cdot \mathbf{grad} \cdot \mathbf{u} \cdot \mathbf{n} \, ds$  by Green's formula, so that :

$$E(u) = \int_{C(L,n,A)} grad u \cdot n \, ds = -\int_{S(L)} grad u \cdot n \, ds.$$

(The last equality is obtained by applying formally Green's formula to  $\int_{\Omega(L,H)} -\Delta u \, dx \, dy \, dz = 0$ ). E(u) is therefore the electrical flux on the bottom plate.

The main difficulty of the numerical treatment of the problem is the difference in scales of  $a^2$  (area of each of the contact surfaces), b (periodicity of the contacts), and H (thickness of the electrolyte) The values of these parameters are typically of the order:  $a^2 = 10^{-14} \text{ m}^2$ ,  $b = 10^{-5} \text{ m}$ ,  $H = 10^{-4} \text{ m}$ . Hence, if a straightforward (non-adaptive) mesh is used for the discretisation of the physical domain, the number of unknowns could reach  $10^{10}$  which is unreasonable even on a modern supercomputer such as the Cray2. We shall therefore study the mathematics of this problem in order to simplify it as much as possible, and also to get an idea of the behaviour we should expect from the numerical solution.

First, it is easy to see that we can restrict ourselves to the study of E(u) on a domain  $\Omega(1,d)$  e.g. of dimensions L' = 1 and d =  $\frac{H}{L}$  since the coefficient  $\alpha$  is left unchanged by such a transformation. (Note that the contact area has also been transformed by a homothecy of coefficient 1/L). The domain we consider is similar to the one shown on Figure 1, with L = 1 and H = d. We still denote by a<sup>2</sup> the area of one contact and by A<sup>2</sup> = n<sup>2</sup> a<sup>2</sup> the total contact area (with A  $\leq$  1), and assume that x=0 and y=0 are axes of symmetry of the contact areas. We denote by b =  $\frac{1}{n}$  the side of one elementary contact cell. Because of the periodicity of the problem, for u solution to Problem (2), we have :

$$\mathbf{E}(\mathbf{u}) = \mathbf{n}^2 \mathbf{e}(\mathbf{u})$$

where :

$$e(u) = \int_{\Omega(b,d)} \|\mathbf{grad} \ u\|^2 \ dx \ dy \ dz,$$

and  $\Omega(b,d) = ]0,b[x]0,b[x]0,d[$ . Let  $u(x,y,z) = v(\frac{x}{b}, \frac{y}{b}, \frac{z}{d})$  where  $u_1$  is defined from  $\Omega(1,1)$  in IR. In the sequel, we shall denote by  $\Omega = \Omega(1,1)$  the unit cube. Then :

$$\int_{\Omega(\mathbf{b},\mathbf{d})} \|\mathbf{grad} \ \mathbf{u}\|^2 \ d\mathbf{x} \ d\mathbf{y} \ d\mathbf{z} = \int_{\Omega} \left[ d \left\{ (\partial_{\mathbf{x}} \mathbf{v})^2 + (\partial_{\mathbf{y}} \mathbf{v})^2 \right\} + \frac{b^2}{d} (\partial_{\mathbf{z}} \mathbf{v})^2 \right] d\mathbf{x} \ d\mathbf{y} \ d\mathbf{z}$$

Hence, using the periodicity of the solution to (2),

$$e(u) = \underset{v \in K_A}{\operatorname{Min}} \int_{\Omega} \left[ d \left\{ (\partial_x v)^2 + (\partial_y v)^2 \right\} + \frac{b^2}{d} (\partial_z v)^2 \right] dx dy dz,$$

where  $K_A = K(1,1,1,A) = \{v \in H^1(\Omega) | v \equiv 0 \text{ on } S(1) = [0,1]^2, \text{ and } v \equiv 1 \text{ on } C_A = C(1,1,A)\}$ . So that :

(3) 
$$I = \frac{1}{d} \underset{v \in K_A}{\operatorname{Min}} \int_{\Omega} \left[ n^2 d^2 \left\{ (\partial_x v)^2 + (\partial_y v)^2 \right\} + (\partial_z v)^2 \right] dx dy dz.$$

We will now study the behaviour of I with respect to the three following parameters:

n : number of elementary cells in each direction (with  $n = \frac{1}{b}$ ) i.e. periodicity of the contacts in each

direction)

A : square root of the global contact area, (with  $A^2 = n^2 a^2$ )

d: thickness of the material

#### 4. Mathematical study of the the solution as $n \to +\infty$ .

Here we take fixed A and d, and study the variation of E(u) with respect to n. This will give us an idea of what the potential looks like in the case of many small contact areas. We consider formulation (3) of the problem to be solved, i.e. the minimisation of the functional :

$$F_n(v) = \int_{\Omega} \left[ n^2 d^2 \left\{ (\partial_x v)^2 + (\partial_y v)^2 \right\} + (\partial_z v)^2 \right] dx dy dz$$

over the set  $K_A$ . We denote by  $u_n$  the function of  $K_A$  which minimizes  $F_n$ . Hence :

$$I = \frac{1}{d} \min_{v \in K_A} F_n(v) = \frac{1}{d} F_n(u_n)$$

By considering the particular function  $w \in K_A$ ; w(x,y,z) = z in  $\Omega$ , we get a first easy estimation :  $F_n(u_n) \le F_n(w) = 1$ . We also get a lower bound by noticing that :

$$F_n(v) \ge \int_{\Omega} (\partial_z v)^2 dx dy dz = \int_E (\partial_z v)^2 dx dy dz,$$

where E = {(x,y,z) ; v(x,y,1)=1,  $z \in [0,1]$ }. Therefore, by the Cauchy-Schwarz inequality,  $F_n(v) \ge A^2$ . Hence :  $A^2 \le F_n(u_n) \le 1$ .

**Lemma**: Let  $u_n = \operatorname{Argmin}_{K_A} F_n$ . Then  $u_n \to u^*$  in  $H^1(\Omega)$ , where  $u^*$  is defined on  $\Omega$  by :  $u^*(x,y,z) = z$ .

*Proof*: Let  $u_n$  minimize  $F_n$ ;  $u_n$  is bounded in  $H^1(\Omega)$ . We can therefore extract a subsequence, still denoted  $u_n$ , which converges to a limit  $u^*$  in  $H^1(\Omega)$  for the weak topology, and in  $L^2(\partial\Omega)$  for the strong

topology. Since  $F_n(u_n) \le 1$ ,  $\partial_x u_n$  and  $\partial_y u_n$  tend to 0 in  $L^2(\Omega)$  as n tends to  $+\infty$ , and  $\partial_x u^* = \partial_y u^* = 0$ . The weak convergence of  $u_n$  in  $H^1(\Omega)$  implies that :

$$\limsup_{n \to +\infty} |\partial_z u_n|_2 \le (F_n(u_n))^{1/2} \le 1 = |\partial_z u^*|_2 \le \liminf_{n \to +\infty} |\partial_z u_n|_2$$

where  $|.|_2$  denotes the  $L^2(\Omega)$  norm. Therefore,  $|\partial_z u_n|_2$  tends to  $|\partial_z u^*|_2$  (= 1) as n tends to  $+\infty$ . Hence  $|\text{grad } u_n|_2$  tends to  $|\text{grad } u^*|_2$  and the whole sequence  $u_n$  converges to  $u^*$  where  $u^*(x,y,z) = z$  in  $H^1(\Omega)$ , for the strong topology.

The interpretation of this result is that, whatever the global contact area (even if it is much smaller than 1) and whatever the thickness of the material, the electric current will, when the number of cells increases, tend to the current one would get with a uniform contact of maximum size (Area  $(C_A) = 1$ ) at the top.

Let us now study the behaviour of  $v_n = z - u_n$  (i.e. the error between the limit potential and the actual one) as n grows. Problem (3) formulated with  $v_n$  becomes :

(4) Find 
$$v_n \in L_A = \{w \in H^1(\Omega) ; w \equiv 0 \text{ on } S(l), \text{ and } w \equiv 0 \text{ on } C_A\}$$
  
such that  $J_n(v_n) \leq J_n(w) \forall w \in L_A$ ,

where  $J_n(w) = \int_{\Omega} [n^2 d^2 \{(\partial_X w)^2 + (\partial_y w)^2\} + (\partial_z w)^2 + 2 \partial_z v] dx dy dz$ . Note that  $F_n(u_n) = 1 + J_n(v_n)$ . It is clear, from the above study of  $u_n$ , that  $v_n \to 0$  in  $H^1(\Omega)$  when  $n \to +\infty$ . Also,  $J_n(v_n) \to 0$  when  $n \to +\infty$ , and  $J_n(v_n) < 0$ . We now prove that  $F_n(u_n)$  tends to 1 (or  $J_n(v_n)$  to 0), when n tends to infinity, with the order  $\frac{1}{n}$ ; more precisely:

**Proposition**: There exist  $C_1$  and  $C_2$  real positive constants such that:  $1 - \frac{C_1}{n} \le F_n(u_n) \le 1 - \frac{C_2}{n}$  for n large enough.

#### Proof:

The proof of this proposition is decomposed into two steps. First we introduce the space :

$$M_A = \{ w \in L_A ; \int_{\Omega} \partial_z v \, dx \, dy \, dz = -1 \};$$

then, for any w in MA, we introduce :

$$p(w) = \int_{\Omega} \left[ (\partial_{x} w)^{2} + (\partial_{y} w)^{2} \right] dx dy dz,$$
$$q(w) = \int_{\Omega} (\partial_{z} w)^{2} dx dy dz.$$

First we note that :

$$J_n(v_n) = \underset{v \in M_A}{\operatorname{Min}} \underset{\lambda \in IR}{\operatorname{Min}} J_n(\lambda v).$$

An easy calculation then yields that, for a given  $w \in M_A$ :

$$\underset{\lambda \in IR}{\text{Min } J_n(\lambda w)} = \frac{-1}{n^2 p(w) + q(w)}$$

Therefore, for any given w in MA,

$$F_n(u_n) \leq 1 - \frac{1}{n^2 p(w) + q(w)}$$

Let us now study the behaviour of the term  $n^2p(w)+q(w)$  with respect to  $w \in M_A$ ; let  $0 \le \epsilon \le 1$  and let  $w_{\epsilon}$  be defined on  $\Omega$  by:

$$w_{\varepsilon}(x,y,1-z) = w(x,y,\frac{1-z}{\varepsilon}) \text{ if } z \in [0,\varepsilon],$$
$$w_{\varepsilon}(x,y,z) = 0 \quad z \in [0, 1-\varepsilon].$$

In other words, we obtain  $w_{\mathcal{E}}$  by "compressing" w towards the contact surface. Let us compute the minimum of :  $n^2 p(w_{\mathcal{E}}) + q(w_{\mathcal{E}})$  with respect to  $\varepsilon$ . Clearly,  $n^2 p(w_{\mathcal{E}}) + q(w_{\mathcal{E}}) = \varepsilon n^2 p(w) + \frac{1}{\varepsilon} q(w)$ , the minimum of which is reached for  $\varepsilon = \frac{1}{n} \sqrt{\frac{q(w)}{p(w)}}$ , i.e. :

(6) 
$$\min_{\varepsilon \in IR} [n^2 p(w_{\varepsilon}) + q(w_{\varepsilon})] = 2 n \sqrt{p(w)} q(w)$$

Therefore, for any given  $w \in M_A$ , and for any n such that  $n \ge \sqrt{\frac{q(w)}{p(w)}}$ , we have:  $F_n(u_n) \le 1 - \frac{1}{2} - \frac{1}{2}$ 

$$F_n(u_n) \le 1 - \frac{1}{2 n} \frac{1}{\sqrt{p(w) q(w)}}.$$

Hence the existence of the constant C<sub>2</sub>.

and

In order to prove the lower bound, we prove that there exists a constant  $\beta > 0$ , such that  $p(w) q(w) \ge \beta$  for any  $w \in M_A$ . The existence of such a constant and equation (6) yield :  $F_n(v_n) \ge 1 - \frac{1}{2n} \frac{1}{\sqrt{\beta}}$  hence

$$C_1 = \frac{1}{2\sqrt{\beta}}$$

We prove the existence of  $\beta$  by contradiction : assume such a constant does not exist, then there exists a sequence  $(w_n)_{n \in IN}, w_n \in M_A$ , such that  $p(w_n) q(w_n) \rightarrow 0$  when  $n \rightarrow +\infty$ . By Cauchy Schwarz' inequality, we have :

$$q(w_n) = \int_{\Omega} (\partial_z w_n)^2 \, dx \, dy \, dz \ge \iint_{\Omega} \partial_z w_n \, dx \, dy \, dz = 1,$$

so that  $p(w_n) \to 0$  when  $n \to +\infty$ . Let  $\gamma_n \ge 1$  and define  $\overline{w}_n$  from  $[0,1]^2 x[1-\gamma_n,1] \to IR$  by:

$$\overline{\mathbf{w}}_{n}(\mathbf{x},\mathbf{y},\mathbf{1}-\mathbf{z}) = \mathbf{w}_{n}(\mathbf{x},\mathbf{y},\frac{\mathbf{1}-\mathbf{z}}{\gamma_{n}}).$$

Let  $\bar{p}(\bar{w}_n) = \int_{[0,1]^2 x[1-\gamma_n,1]} [(\partial_x \bar{w}_n)^2 + (\partial_y \bar{w}_n^2] dxdydz and \bar{q}(\bar{w}_n) = \int_{[0,1]^2 x[1-\gamma_n,1]} (\partial_z \bar{w}_n)^2 dxdydz;$ clearly,  $\bar{p}(\bar{w}_n) = \gamma_n p(w_n)$ , and  $\bar{q}(\bar{w}_n) = \frac{1}{\gamma_n} q(w_n)$ . Choose  $\gamma_n = q(w_n) (\geq 1)$ , so that  $\bar{q}(\bar{w}_n) = 1$ . Again, since  $\bar{p}(\bar{w}_n) \bar{q}(\bar{w}_n) = p(w_n) q(w_n) \rightarrow 0$  when  $n \rightarrow +\infty$ , we have  $\bar{p}(\bar{w}_n) \rightarrow 0$  when  $n \rightarrow +\infty$ . Let  $\bar{w}_n$  be the restriction of  $\bar{w}_n$  to  $\Omega$ ; by definition of  $\bar{w}_n$ ,  $\bar{w}_n$  satisfies:  $\bar{w}_n = 0$  on  $C_A$ , and  $\int_{z=1}^{z=1} w_n dx dy dz = -1$ . Now,  $\bar{w}_n \rightarrow \bar{w}$  when  $n \rightarrow +\infty$ , in in H<sup>1</sup>( $\Omega$ ) for the weak topology, where  $\bar{w}$  is a function defined in  $\Omega$ , which satisfies:  $p(\bar{w}) = 0$ , so that  $\bar{w}$  depends only on z. Since  $\bar{w} = 0$  on  $C_A$ ,  $\bar{w} (x,y,1) = 0$ , for  $(x,y) \in ]0,1[x ]0,1[$ . But this is in contradiction with the fact that  $\int_{z=1}^{z=1} w_n dx dy dz = -1$ .

We have just proved that for a large number of contacts the difference between the electric energy we would get with the maximum area of contact (= 1) and the one we have with the area A made out of n subareas is of the order  $\frac{1}{n}$ .

This estimate will be very useful in order to check the accuracy of the numerical solution, which we now proceed to.

**Remark :** In this section, we studied the behaviour of the solution when n tends to infinity. Another point of interest would be the behaviour of the solution as the total area A of the contacts tends to 1. When A tends to 1, the solution of the problem tends to  $u^*$  such that  $u^*(x,y,z) = z$  (the proof of this result is similar to the proof of the above lemma). The behaviour of the difference is, however, more complex because it strongly depends on the shape of A (as the study of the dependency of the solution with respect to n shows).

#### 5. Numerical Implementation and Results

For the numerical implementation, we consider the contact area  $C_A$  to be a square with sides of length A parallel to the x and y axes. For reasons of symmetry, and in order to save CPU time and memory, problem (3) can be solved by considering functions which satisfy the following equations :

 $\frac{1}{4} n^2 d^2 \left[ (\partial_x v)^2 + (\partial_y v)^2 \right] + (\partial_z v)^2 = 0 \text{ in } \Omega,$ v = 1  $\Gamma_A = \{ (x, y, z) ; 1 - A \le x \le 1, 1 - A \le y \le 1, z = 1 \}$ v = 0, on  $\Gamma_0 = \{ (x, y, z) ; 0 \le x \le 1, 0 \le y \le 1, z = 0 \}$ grad v . n = 0 on  $\partial \Omega \setminus (\Gamma_A \cup \Gamma_0)$ 

The computational domain being as shown in Figure 2, we divide it into four subdomains which are numbered as follows:

subdomain 1 :  $[0,1-A] \ge [0,1-A] \ge [0,1]$ ; subdomain 2 :  $[1-A,1] \ge [0,1-A] \ge [0,1]$ subdomain 3 :  $[1-A,1] \ge [0,1-A] \ge [0,1]$ ; subdomain 4 :  $[1-A,1] \ge [1-A,1] \ge [0,1]$ 



Figure 2

The x and y dimensions of subdomain 4 are going to be, for cases which are of interest for the physical modeling, of very small size. Typically,  $1 - A = 10^{-2}$ . This is a major difficulty in the treatment of the

problem by the finite element method, since the accuracy of the discrete solution will degrade if the finite elements are of very different sizes.

A possible remedy to this problem is to increase the number of mesh points in x and y in subdomain 1, 2 and 3, and to adapt the grid points so that the distance between two grid points of the top faces of subdomains 1, 2 and 3 is of the order of the distance between two grid points on the contact area (i.e. subdomain 4). Let m be the number of grid points in the x and y direction on the contact area (subdomain 4) and M the number of points in the x and y direction for subdomain 1.

We define  $h: [0,1-A] \rightarrow [0,1-A]$  by :

$$h(x) = \frac{a}{m} \left(\frac{x}{1-a}\right)^3 - \left(1 + \frac{a}{m}\right) \left(\frac{x}{1-a}\right)^2 + 2\frac{x}{1-a}$$

and take the coordinates of the grid points of subdomain 1 to be :

$$\xi_i = h(x_i)$$
 where  $x_i = \frac{i(1-a)}{M}$ ,  $i = 1, ..., M$ ,  
 $\eta_j = h(y_j)$  where  $y_j = \frac{j(1-a)}{M}$ ,  $j = 1, ..., M$ .

As we show later on, in order to get accurate results, the mesh needs to be adapted so that it be very fine near the contact area. We choose the same discretisation in z on all four subdomains; the adaptive step size in z is chosen so that the mesh size of the finite element is of order  $\frac{1}{n}$  near the contact area, since the mathematical estimate of section 4 shows that the difference  $u_n - z$  is of order  $\frac{1}{n}$ .

Let P be the number of elements in the z direction. Then the coordinates of the mesh points in direction z are defined by :

$$\zeta_{\mathbf{k}} = \frac{1}{n} z_{\mathbf{k}}^{3} - (1 + \frac{1}{n}) z_{\mathbf{k}}^{2} + 2 z_{\mathbf{k}}$$
, where  $z_{\mathbf{k}} = \frac{1}{P}$ , for  $\mathbf{k} = 1, ... P$ .

The programming was done within the ASTRID environment (Gruber et al.(1989)). The ASTRID code is a finite element code which was developped for the high speed reoslution of several engineering problems on the CRAY2. We used the direct LL<sup>T</sup> solver of ASTRID to solve the Laplace problem. Note than an iterative solver would allow us a much finer mesh, since the memory requirement of an iterative solver is much lower than that of a direct solver. Unfortunately, however, problem (7) leads to a very illconditioned matrix so that an iterative solver does not perform well when n becomes large.



Figure 3

The first computations were carried out on a Silicon Graphics workstation, but even with the adapted mesh, the numerical results were not accurate because of the limited size of the mesh. For a mesh of M = 6, m = 2 and P = 8, we get, for fixed  $A = 10^{-2}$  and  $d = 10^{-2}$ ), a behaviour of the effective resistance for large values of n in  $\frac{1}{n^2}$ , and this, we know by the mathematical estimate of Section 3, is not accurate. What happens is that, for a mesh which is not fine enough, the "compressed" function  $w_{\varepsilon}$  that we introduced in Section 4 is not "seen" by the mesh; the minimum of the discrete problem is attained by the function w, but does not take the functions  $w_{\varepsilon}$  into account, which explains the behaviour in  $\frac{1}{n^2}$  of the effective resistance.

Computations were then performed on the Cray 2 with a mesh defined by M = 15, m = 5 and P = 20 and 25 (in order to show the influence of the refinement of the mesh). The first set of runs was performed for fixed A and d, with varying n. This enables us to compute the constants of the asymptotical behaviour of  $E_n(u_n)$  (and thus of the effective resistance) with respect to  $\frac{1}{n}$ . A plot of the resistance increase versus n is shown in Figure 3.

The logarithm of the resistance increase coefficient  $\alpha$  is shown in Figure 4. It can be seen, even with a finer mesh (M = 15, m =5, P = 25), that we have not yet reached the asymptotic behaviour of  $\alpha$  (i.e. for lage values of n) which is expected from the mathematical study. The asymptotical line is plotted to show the difference of slopes for the coarse mesh, the finer mesh and the ideal behaviour (slope of -1).

Assuming that the mathematical asymptotical behaviour is already valid for "small" values of n, the equivalent resistance can be modeled by  $\alpha = 1 + \frac{e^{C}}{n}$ , where C = 8.255 is determined numerically. This model was checked numerically by refining the mesh furthermore (M=25, m = 10, P = 40). It can be seen that the curve is now very close to the asymptotic line and the difference between the effective resistance and the homogeneous one is now of the order 1/n. Note that the mathematical analysis which we performed earlier is a very useful tool here to determine the refinement level of the grid which we need in order to obtain reasonable accuracy of the solution.



The most accurate results (or the mathematical asymptotical model) yield, for A=.01 and d=.01) a resistance increase of 32 for n=100 and 1.22 for n=1000. It is therefore obvious that material technology for SOFC's should aim at obtaining as many "active regions" as possible, especially if the overall area of contact is small.

The behaviour of  $\alpha$  with respect to A (area of the contact) is shown in Figure 5. Again, the refinement of the mesh influence the results. Figure 6 shows the logarithm of the coefficient  $\alpha$  with respect to the logarithm of A. The numerical results tend to show that the resistance increases as  $A^{-k}$ , where k is close to (but less than) 1.



#### **Conclusions**

We studied here the influence of the contact area on the effective resistance of an electrolytic membrane. It was shown mathematically that, for any value of the total contact area, the effective resistance tends to the homogeneous one when the number of contact points become large. The behaviour of the difference between the effective resistance and the homogeneous one was studied, and allowed us to check the accuracy of the numerical results. These results will be helpful to the electrochemists for a better understanding of the phenomena which lead to an increase of resistance of the electrolyte.

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Figure 6



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# Cathodic O<sub>2</sub> Reduction Impedance at a known 3-Phase Boundary Length

#### J. Van Herle (Switzerland)

#### <u>Summary</u>

The O<sub>2</sub> reduction at the cathode of a SOFC (YSZ as the solid oxide ion conductor) plays a major role in the overall performance of this type of fuel cell. In this work, this cathode reaction was studied on geometrically precisely defined gold electrodes : the zone where the reaction can occur is restricted and known. Impedance spectroscopy enabled us to model our system with an equivalent electrical circuit. Further investigation is being undertaken in order to come up with a conclusive physical interpretation of the model.

#### <u>Experimental</u>

Squares of 25 x 25 x 1 mm of 6 mole%  $Y_2O_3$ -ZrO<sub>2</sub> (6YSZ) from the Swiss company METOXIT were purchased. X-ray diffraction reveals the material to be purely cubic.

By PVD and photomasking techniques, a precursor gold electrode of precise geometry is deposited onto the ceramic. Sizes of the electrodes used here were  $23.0 \times 8.0 \text{ mm}$  and  $23.0 \times 4.0 \text{ mm}$ .

The precursor electrode is densified by plating from a commercial gold bath. Making the electrodes dense (impermeable to gases) will force the  $O_2$  reduction reaction to occur only at the periphery of the electrode.

The typical thickness of the plated layer is about 30  $\mu$ m. Theoretical thickness of the layer (as calculated from the weight deposited) and measured thickness (by SEM and microstylus) coincide very well. Furthermore, from SEM pictures the appearance of the layer is dense (see Figure 1). The sharpness of the edge of a plated gold electrode is about 2 to 3  $\mu$ m (Figure 1).



<u>Figure 1.</u> SEM image of a dense gold electrode. Magnif. 500x.

Two types of cells were used (Figure 2) :

- A) a symmetrical type where two dense gold electrodes are aligned on opposite faces of the square electrolyte sample.
- B) an asymmetrical type with a dense gold working electrode on one face and a porous silver counterelectrode on the other face.



Contacting to the electrodes was made with pure silver and pure gold wires ( for the silver and gold electrodes respectively ).

The cell is mounted into a tubular oven that can be closed off. An air flow of 100 ml/min was maintained during all the measurements. Care has to be taken with the heating rate : it should not exceed 150°C/hr, otherwise the dense gold electrode will delaminate.

#### Impedance measurements and model

Impedance measurements were taken typically at 700-800°C between  $10^{-2}$  and 2.10<sup>4</sup> Hz (V<sub>FRS</sub> = 10 mV) with a Solartron 1253 Frequency Response Analyser (FRA), connected to the cell through the Solartron 1286 Electrochemical Interface (EI). The 1253 FRA and 1286 EI are interfaced to a HP computer, that collects, stores and analyses the data.

In one occasion, the temperature dependence of the impedance spectra between 600 and 900°C was followed.

In another case, several biases between 25 and 500 mV were superimposed on the ac signal and the impedance response measured. In this case, the gold electrode was the working one (cathode). A dense electrode cannot be used as an anode, because O, evolution will literally crack up the whole electrode surface. This was demonstrated with an asymmetrical cell by applying purposely a high anodic potential to the dense gold electrode for a prolonged time (e.g. 500 mV for 15 minutes). The result is



obvious from SEM images (Figure 3). It follows that the reaction length now available (periphery of the electrode plus all the cracks in the electrode) for - O<sub>2</sub> the reverse reaction reduction at the gold electrode - is much higher than before (only periphery of the electrode), and thus the should impedance decrease markedly, which is indeed clearly observed.

<u>Figure 3.</u> SEM image of the gold electrode after destruction by anodic O<sub>2</sub> evolution. Magnif. 600x.

Two stages are clearly visible in the impedance spectrum (Figure 4).

It was possible to fit all the impedance data with an equivalent electrical circuit as proposed in *Figure 5*. The parallel connection of a resistance and a CPE ("constant phase element") is known as a ZARC element, which is characteristic for a depressed semicircle, as observed in the spectrum.

The error between experiment and model lies at about 2% (see Figure 4).



<u>Figure 4.</u> A typical impedance speatrum. Asymmetrical cell, 700 C. Evidence for the agreement between experiment (points) and model (solid line).

Further investigation will allow to attribute the parameters of the electrical circuit to the reaction mechanism ; so far following preliminary facts have resulted :

1) despite being dense, the whole electrode area is involved in both stages of the model, since the capacitances of the 23 x 8mm electrode and the 23 x 4mm electrode relate exactly as 2 to 1.

- 2) the resistance  $R_1$  follows an Arrhenius law with temperature (with an activation energy of 1.26 eV), whereas  $R_2$  doesn't.
- 3) the resistance  $R_1$  remains invariant with bias, whereas  $R_2$  markedly increases with increasing bias.
- 4) R<sub>2</sub> makes out more than 80% of the total impedance.
- 5) capacitances involved are high (on the order of mF).
- 6) at 800°C, one calculates the impedance of the O<sub>2</sub> reduction at a gold electrode to about 100  $\Omega/cm$  of TPB length.

$$Z=R_{s}+\left(\frac{1}{R_{1}}+\frac{1}{\sigma_{1}},(i\omega)^{\alpha_{1}}\right)^{-1}+\left(\frac{1}{R_{2}}+\frac{1}{\sigma_{2}},(i\omega)^{\alpha_{2}}\right)^{-1}$$

For the spectrum in Fig. 4, following values for the fitting parameters were used :

R <sub>g</sub>	10.93	
n R <sub>1</sub>	151.8	
σ1	919.6	
a <sub>1</sub>	-0.728	
angle 24.5°		
R <sub>2</sub>	1030.4	
σ,	174.4	
az	-0.876	
angle 11.1°		





Figure 5. A possible equivalent circuit. "CPE" denotes a constant phase element. R1 is the high frequency resistance.

### 8. Oxygen Stoichiometry and Transport in LSM

I.G. Krogh Andersen, E. Krogh Andersen, S. Habekost, P. Norby, E. Skou, T. Jakobsen, B. Zachau-Christiansen, K. West & S. Skaarup (Denmark)

To establish a satisfactory model of the SOFC oxygen electrode it is nescessary to know:

- 1. The electronic- and oxygen ion conductivity as function of oxygen stoichiometry.
- 2. The oxygen stoichiometry as function of oxygen partial pressure.
- 3. The relation between oxygen stoichiometry and unit cell dimensions.
- 4. The phase stability.

In order to evaluate these properties the following methods has been applied to a range of lanthanum strontium manganites with different strontium contents and prepared by different synthetic routes:

- 1. Linear Sweep Voltammetry
- 2. Thermogravimetry
- 3. Chemical Analysis
- 4. Diffraction Studies.

#### 1. Linear Sweep Voltammetry

In linear sweep voltammetry is used the galvanic cell:

Pt,O<sub>2</sub> | YSZ | Pt, LSM

where a sample of LSM is enclosed in a sealed YSZ compartment.

The oxygen partial pressure in the compartment is determined by the potential difference between the platinum electrodes of which one is exposed to air and the other is inside the sealed compartment containing the sample to be investigated. The main contribution to the current flowing into or out of the cell corresponds to the transfer of oxygen to the LSM compound. Therefore, if the cell voltage is changed continuously the current will (after correction for the capacity of the gas volume in the cell and a small leak current) reflect the change in average stoichiometry of the sample. Because of the limited range of solid state diffusion the current increases with decreasing sweep rate until a limiting behavior is obtained at low sweep rates.

In fig 1 voltammograms are shown for  $La_{0.85}Sr_{0.15}MnO_{3+\delta}$  and  $LaMnO_{3+\delta}$  in the potential range from -0.4V to 0.05 V vs air i.e. with oxygen partial pressures in the range from  $10^{-6}$  atm to 1 atm.







Fig.2 Stoichiometry of La<sub>0.85</sub>Sr<sub>0.15</sub>MnO<sub>3</sub> and LaMnO<sub>3</sub> at 990°C as function of electrode potential and oxygen pressure.

From the sweeps the change in stoichiometry with electrode potential is obtained by numerical integration and subtraction of the gas phase capacity [1]. If the composition at -0.4 V is assumed to have the stoichiometry  $(La,Sr)MnO_3$  the absolute stoichiometry can be calculated and is shown in fig 2 in comparison with results obtained from thermogravimetry.

#### 2. Thermogravimetry.

In the thermogravimetric investigations a c. 50 mg sample is placed in a thermobalance and heated in an atmosphere with an oxygen partial pressure of c.  $10^{-6}$  atm. When the weight of the sample has stabilized the partial pressure of oxygen in the surrounding atmosphere is changed to 0.5 atm and the change in weight is followed as function of time. The measurements allow a determination of both the stoichiometry change and the oxygen diffusion kinetics.

Fig. 3: Weigth gain vs. time of a 49 mg. sample of LaMnO<sub>3+6</sub> after exposing the sample to 0.5 atm oxygen partial pressure. The initial part of the curve can be fitted with a square root law corresponding to diffusion of oxygen into the crystal.



In fig 3 is shown an example obtained for LaMnO<sub>3+ $\delta$ </sub> at 800 °C. The initial part of the curve can be fitted with a square root dependency. At longer times, deviations are observed probably caused by the intersection of the two oxygen diffusion fronts from both sides of the crystallites, thus invalidating the assumption of infinite diffusion. Diffusion coefficients can be deduced from the slope when the surface area of the sample is known, a task still in progress. Activation energies can be determined, however, without knowledge of the surface area from the temperature dependency of the slope of the square root plot and is shown in fig 4 for a sample of La<sub>0.85</sub>Sr<sub>0.15</sub>MnO<sub>3+ $\delta$ </sub>.

Comparison with results obtained by linear sweep voltammetry on samples of the same preparation shows good agreement but the change in stoichiometry is somewhat lower than results reported in the literature for samples with similar compositions.
Fig 4: Plot of diffusion rate as determined from plots as in fig 3 as function of reciprocal absolute temperature. From the slope the activation energy for oxygen diffusion can be determined.



#### 3. Chemical Analysis.

By linear sweep voltammetry and thermogravimetry only changes in the oxygen stoichiometry can be determined. To determine absolute stoichiometries knowledge of the absolute stoichiometry at a specific oxygen partial pressure is needed. In the literature nominal stoichiometry (i.e.  $O_{3.00}$ ) is usually assumed a an oxygen partial pressure of  $10^{-9}$  to  $10^{-6}$  atm where the composition is independent of the partial pressure, but no direct proof of this has been given. It was therefore decided to try to determine the absolute composition of selected samples equilibrated at different oxygen partial pressures. Physical methods (atomic absorption and XRF) was judged to be too inaccurate so a chemical analysis was attempted. The methods we have found most reliable are reported separately, so only the principles will be described here.

The total content of manganese in the sample is determined after reduction of all manganese to Mn(II). The amount of Mn(II) is then determined by titration with permanganate in a pyrophosphate solution.

The sum of Mn(III) and Mn(IV) is determined by reduction with strong hydrochloric acid and subsequent determination of the liberated chlorine by iodometry. From those two determinations the ratio between Mn(IV) and Mn(III) in the sample can be determined and the total composition calculated for lanthanum manganites, as lanthanum can be assumed only to be present in oxidation state III. If the ratio between lanthanum and strontium in the sample is known also lanthanum strontium manganites can be analyzed this way. Lanthanum can be determined by precipitation with fluoride and a potentiometric titration of the remaining fluoride with lanthanum nitrate, but strontium interferes with the determination. This problem has not been solved so far.

Analysis of La  $MnO_3$  synthesized from acetates and calcined in air showed the composition  $La_{.96}Mn_{.96}O_{3.00}$  and a hexagonal phase. The same sample annealed in nitrogen analyzed to  $La_{1.00}Mn_{1.00}O_{3.00}$  and an orthorhombic phase.

These preliminary results indicate that at least for lanthanum manganites the assumption of stoichiometric composition at the plateau in the TG vs oxygen partial pressure curves seems justified.

#### 4. Diffraction Studies.

Information about oxygen nonstoichiometry can also be obtained from powder diffraction studies where the occupancies of the different constituents are determined. Neutron- and X-ray powder diffraction studies have been performed on LaMnO<sub>3+δ</sub> and on La<sub>.85</sub>Sr<sub>.15</sub>MnO<sub>3+δ</sub> and the occupancies determined by a Rietveld profile analysis. No interstitial oxygen has been found but lanthanum ion vacancies in accordance with the findings by Tofield and Scott [2]. Comparison with occupancies determined by chemical analysis is in progress.

Unit cell dimensions and phases have also been determined by X-ray diffraction. When the hexagonal LSM is annealed in nitrogen a phase shift to the orthorhombic phase is observed accompanied with a change in unit cell dimensions. For a pure lanthanum manganite the volume change is 3.5%. Work is going on to determine the critical oxygen partial pressure as well as the importance of the phase change for the oxygen diffusion rate.

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# 9. Address Directory of the Participants in the SOFC Micromodelling Activity

### Denmark

Eivind SKOU, Odense U, Campusvej 55, DK-5230 Odense M + 45 / 6615 8600 / fax 6615 8780 Torben JACOBSEN, TU, Fys.kem.Inst., DK-2800 Lyngby + 45 / 4593 2380 X2437 / fax 4593 4808

### Italy

Vincenzo ANTONUCCI, CNR-TAE, via S.Lucia 39, I-98126 Pistunina-Messina + 39 / 90271 4575 / fax 9060 1011 Nicola GIORDANO, CNR-TAE, via S.Lucia 39, I-98126 Pistunina-Messina + 39 / 90271 4575 / fax 9060 1011

#### Japan

Toshihiko SAITO, SANYO ELECTRIC Co,1-18-13 Hashiridani, Hirakata City, Osaka 573 + 81 / 72041 1264 / fax 72041 0302

# The Netherlands

Karel DE VRIES, U Twente, PO Box 217, NL-7500 A-F Enschede + 31 / 5389 2996 / fax 5335 6024

#### Norway

Asbjørn SOLHEIM, SINTEF, N-7034 Trondheim + 47 / 759 4054 / fax 759 4083 Ivar DAHL, SI, PO Box 124 Blindern, N-0314 Oslo3 + 47 / 245 2685 / fax 245 2040 Jon Kristian RAMSVIK, NTH, N-7034 Trondheim + 47 / 759 3974 / fax 759 4083 Erik SANDVOLD, NORSK HYDRO, Postboks 2560, N-3901 Porsgrunn + 47 / 356 2254 / fax 356 3263 Reidar TUNOLD, NTH, N-7034 Trondheim + 47 / 759 4043 / fax 794 4513

# Switzerland

Raphaèle HERBIN, U de Savoie, Lab. Mathématique, F-73376 Le Bourget-du-Lac + 33 / 7975 8716 / fax 7975 8742 Michel KLEITZ, LIES-G, BP 75, F-38402 St Martin d'Hères + 33 / 7682 6566 / fax 7682 6670 Augustin McEVOY, ICP2, EPFL, CH-1015 Lausanne + 41 / 21693 3689 / fax 21693 4111 Helmut TANNENBERGER, 218 La Villette, CH-1450 Le Château de Ste Croix + 41 / 2461 1480 Jan VAN HERLE, ICP2, EPFL, CH-1015 Lausanne + 41 / 21693 2108 / fax 21693 4111

# United Kingdom

Steve RANDALL, BG plc, Watson House, Peterborough Rd, London, SW6 3HN, UK + 44 / 71736 1212 / fax 71731 1648