

On the single chamber solid oxide fuel cells

I. Riess*

Physics Department, Technion-IIT, Haifa 32000, Israel

Received 24 June 2007; received in revised form 11 September 2007; accepted 16 September 2007

Available online 21 September 2007

Abstract

Single chamber solid oxide fuel cells, SC-SOFCs, design and performance is discussed. It is shown that all of them operate on non-selective anodes. They operate on cathodes that become selective only under short residence times. As a result these cells are not functioning as true mixed reactant solid oxide fuel cells (MR-SOFC). The lack of selectivity is a serious drawback. True MR-SOFC can be constructed in ways that make them cheaper in fabrication, providing high power density, high fuel utilization and reduced explosion risk. The fact that SOFCs operate in a single cell is a necessary but not sufficient condition for the proper operation of MR-SOFCs.

The selectivity looked for the anode and cathode is of a special kind. It selects between electrochemical and chemical reactions, preferring the first ones. Results reported here suggest that MR-SOFC can operate only up to $\sim 600^\circ\text{C}$. At these relative low temperatures, materials other than oxides can also be considered for use. Future directions in the needed research in order to develop true MR-SOFCs are discussed.

© 2007 Published by Elsevier B.V.

Keywords: Single chamber SOFC; Mixed reactant SOFC; SOFC; Fuel cell; Selective electrodes; Selectivity

1. Introduction

In a single chamber, or mixed reactant fuel cell (MR-FC), air and fuel are mixed before being introduced into the cell. As the same gas mixture is flushing both the cathode and the anode the symmetry is broken by the use of different materials for the two electrodes. One material is aimed at catalyzing the cathodic reaction and the other the anodic reaction. Both materials should be inert towards the direct chemical full oxidation reaction of the fuel.

This possibility has been demonstrated experimentally in 1961 by Eyraud et al. [1] and few publications that followed for the next 30 years [2–16]. It was shown theoretically that if the electrode were strictly selective as required above, then the cell EMF would equal to that expected in a conventional fuel cell with the cathode exposed to air, the anode to fuel and one of the electrodes being also exposed to the exhaust gases [17]. The significance of these cells is that since air and fuel can be mixed, sealing is not required. This eliminates a serious difficulty in high temperatures solid oxide fuel cells, SOFCs. It also allows to put the cell into a single gas chamber. As a result interest grew

in these single chamber fuel cells and in particular those of the SOFC type (SC-SOFC). An increasing number of experimental results on SC-SOFCs were reported in recent years coming, first, mainly from Hibino et al. [16,18–20] and lately also from other groups, in particular Shao et al. [21–22], Napporn et al. [23–25], Stefan et al. [26], Suzuki et al. [27,28] and quite recently from Buegler et al. [29–31]. For a recent review see Yano et al. [32].

If the SC-SOFC would function as assumed theoretically, i.e. with true selective electrodes, then the advantage of the cell would be much beyond the question of sealing. Since gas separation is not required the solid electrolyte can be made porous [17]. This opens ways for new designs of the SC-SOFC as shown below.

Unfortunately, the SC-SOFC presented to date do not function as expected [33,34]. They seemingly have the correct structure, namely, an element of an SOFC placed in a single chamber with a mixture of reactant gases flushing both electrodes. The SOFC element has the form and composition of a conventional SOFC element: cathode|SE|anode (SE, solid electrolyte) usually in the form of a pellet. Fuel utilization is very low of the order of 1.5% [32]. It is admitted that the anode is not selective and the notion is that the cathode is selective. It will be shown that the cells denoted today as SC-SOFC function actually as normal SOFC. The trick

* Tel.: +972 4 829 5914; fax: +972 4 829 5755.
E-mail address: riess@tx.technon.ac.il.

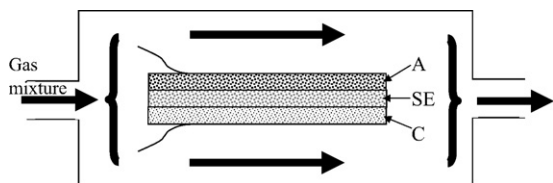


Fig. 1. SOFC planar element. A, anode; SE, solid electrolyte; C, cathode. The SE can be dense or porous.

is to manipulate the gas composition and flow. This works with both hydrocarbons and hydrogen as fuel. Hydrocarbons have the advantage that partial reforming is possible thus allowing to complicate the process making it more liable for misinterpretation.

Here is an example of how the gas composition and flow are handled. Let the gas mixture consist of methane and air. The following limitations are imposed: (a) the fuel oxygen mixture is fuel rich with a ratio: $\text{CH}_4:\text{O}_2=2:1$, instead of the one needed for full oxidation: $0.5:1$; (b) the gas is split, half being directed towards the anode only and the other half towards the cathode only (see Fig. 1); (c) the flow rate is controlled to be high. The anode is not selective and in the gas flushing the anode full oxidation is taking place. However, the limited supply of oxygen assures that only partial reforming occurs ($\text{CH}_4 + 1/2\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2$). This is equivalent to supplying just fuel, of different nature (CO and H_2), to the anode side. The cathode is being flushed with the gas mixture and it is assumed that the cathode is selective. Unfortunately, even the latter assumption is questionable since if it were correct the power output would not depend on the flow rate and fuel utilization could approach 25% instead of 1.5%, as mentioned before. This suggests that the cathode is not selective either.

Since the cells do not function as proper MR-SOFCs the significant advantage that they may have, allowing for completely new cell design, cannot be realized. For the sake of the discussion here we shall denote the cells used to date, as SC-SOFC as they utilize, indeed, a single chamber, and the ones that really allow any mixture of reactants to be introduced into the cell and do not require manipulation of the gas flow, as mixed-reactant-fuel-cells (MR-FCs). We concentrate on the SOFC type MR-FCs and denote them as MR-SOFC.

Section 2 presents the possible new designs for MR-SOFCs. Their advantage over the conventional tubular or planar SOFC design is emphasized. When presenting the more conventional design of SC-SOFC the way the gas flow is manipulated is demonstrated. Section 3 discusses the required catalytic properties of the different layers in the MR-SOFC. In Section 4 results of catalytic properties are presented as measured on a series of materials, mainly the more common ones used in SOFC R&D. This is done in order to screen those that are potentially suitable for use in MR-SOFC. Section 5 discusses the residence time and its possible impact on the selectivity of electrode and calculates the residence time in the various designs. Section 6 is a summary that presents the future activity directions needed for developing a true MR-SOFC to allow making use of its significant advantages.

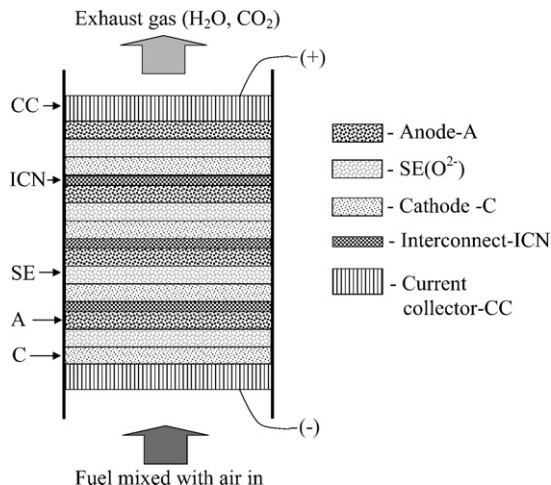


Fig. 2. The MR-SOFC compact stack design [35,36].

2. Different possible designs of SC-SOFCs and MR-SOFCs

2.1. The compact stack design

Fig. 2 exhibits a design suggested in a patent by Priestnall et al. [35,36]. It is based on the idea that the solid electrolyte and not only the electrodes may be porous [17]. In the design of Fig. 2 the layers of the stack, placed one on top of the other, are all, including the solid electrolyte, porous. The same elemental cell is repeated many times. Current collectors are applied only at the ends. The gas mixture of fuel together with air is introduced into one end of the many layer stack and the exhaust gas is coming out at the opposite end.

The element that is repeated contains four layers: anode, SE, cathode and interconnect.

This arrangement has the following significant advantages:

- It is simple and much less expensive to construct than conventional SOFC. Thus rendering the MR-SOFC economically feasible.
- It provides a very high energy density, allowing it to be used in application with limited space, and for large-scale energy conversions.
- It allows for high fuel utilization.
- It allows for a short residence time of the gas mixture. This turns out to be a significant feature on the route to develop layers with the correct catalytic activities and selectivity.
- Reduces explosion risk.

The ease of its construction is demonstrated in Fig. 3. It exhibits the results of a preliminary experiment to prepare a multi ceramic layer stack. The question to be answered in that experiment was: is it possible to sinter and then heat cycle different ceramic layers that have a priori different recommended sintering temperatures and different expansion coefficients, and if this is successful, will the stack be flat or curved. The materials used were $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-x}$ (SSCO) – the cathode, $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{2-x}$ (GDC) – the SE and $\text{NiO} + \text{SE}$ in 50–50 vol. % – the anode. Starch

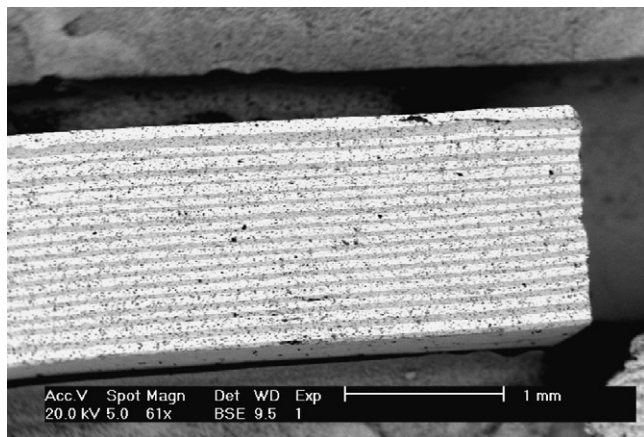


Fig. 3. Fifty-one ceramic layers prepared by tape casting. Cathode, SSCO; SE, GDC; anode, NiO+SE. The anode and SE cannot be distinguished (bright regions). The cathode layers are dark.

3 wt.% (concentration not optimized) was added for generating porosity. No interconnect was applied. The layers were prepared by tape casting. A layer was added after the previous one was dry. Then all layers were sintered together at 1450 °C for 0.5 h after a dwell at 400 °C for 0.5 h and one at 1000 °C for 1 h. Heat cycling five times did not damage the sintered sample. The bright layers in Fig. 3 are the SE and the anode. Both appear with the same color. The dark layer is the cathode. The average layer thickness is 30 μm . The stack consists of 51 layer, i.e. 17 elements of anode|SE|cathode. The layers appear rather flat. When one element is fired it comes out completely curled. At least 15 layers (five elements) are needed in order to obtain a reasonably flat stack. The layers become flat since opposing forces act on the inner layers. For a many layer stack the a-symmetry of forces due to the outer layers has a negligible effect.

Let us estimate the energy density of such a cell. In doing so we shall also determine the residence time of the gas mixture in the cell. We examine the dimension, power output and residence time of a stack according to the design shown in Fig. 2. While the thickness of the layers can be made small there are limitations that have to be taken into consideration.

2.1.1. SE

The SE can be made quite thin, if the ionic transference number, t_i , is unity. This reduces the resistance to ionic current through the SE bulk. In the porous SE a parallel path of ionic motion on the surface of the pores may become significant and also contribute to the ionic conductance [3,37]. However, there is a practical limit to reducing the SE thickness in order to avoid the possibility that the anode and cathode become short circuited accidentally through the pores in the SE.

If $t_i < 1$ then there is an additional lower limitation on the SE thickness. The thickness cannot be made too small as an electronic leakage current may be generated that enhances the overpotential at the electrodes and suppresses the cell EMF [38].

Experience shows that SEs in SOFCs of $\sim 10 \mu\text{m}$ thickness function well and it is anticipated that no contact between the cathode and anode through the pores will occur in the preparation

process. We therefore use from here on 10 μm as a characteristic measure of the SE thickness.

2.1.2. Cathodes and anode

The current in this arrangement is through the low dimension of the electrode layer, i.e. only through a short distance. (Only small lateral currents may exist due to the non-uniformity of the porous SE). From this consideration the electrodes can be made rather thin. However, again there is a need that the electrodes keep the adjacent layers separated. In addition, it is common practice to mix the electrode material with a second phase, that of the SE, in order to enhance the electrode active area. This imposes an upper limit on the electrode thickness. There is no point in making the electrode much thicker than the SE as the SE phase in the electrode will be too thick. We therefore shall take the thickness of the electrodes to be equal to that of the SE.

2.1.3. Interconnect

The interconnect (ICN) has to transfer electrons from the anode to the nearest cathode connected in series. It has, however, three more tasks. First, to keep the adjacent layers separated. Second, to separate the electro-active ionic species on the adjacent cathode and anode so that these species cannot react. If they react it is not an electrochemical reaction that contributes to the cell external current. The reason is that the ionic current (which is in the wrong direction) is short circuited by the ICN. This reaction is thus equivalent to the direct chemical oxidation reaction and wastes fuel. Third, the ICN should separate the possible SE phase added to the two electrodes. For this purpose a thin layer is sufficient. However, for the second one the thickness is dictated by the surface diffusion rate (in the ICN pores) of the electro-active specie. The thickness has to be high with an extended surface diffusion length so that the rate of the corresponding reaction is low compared to the ionic current through the SE. There is no universal answer for that thickness and we assume tentatively that an ICN thickness equal to that of the SE is sufficient.

In view of the former discussion we consider elements consisting of a cathode, SE, anode and interconnect with all four (porous) layers having the same thickness. With the thickness of the SE of 10 μm an element is 40 μm thick. Thus a stack of 100 elements, only 4 mm thick, will provide 50 V under maximum power. A typical current density at maximum power is 1 A cm^{-2} . Thus a stack of 10 cm \times 10 cm area and 0.4 cm thick will provide 5 kW of power. In view of the small volume this is a very high power density to the extent that one has to worry about getting rid of the heat generated in parallel to the electrical energy. That is the reason why we limit the discussion to a module that contains a stack of 100 elements, only.

The residence time, τ_{res} , that is considered below to be of prime importance, is now calculated for that stack of 100 elements. First one has to calculate the fuel and oxygen supply needed to generate 1 A cm^{-2} . This requires a supply of $0.25 \times 10^{-5} \text{ mol O}_2 \text{ cm}^{-2} \text{ s}$ per element, i.e. $0.056 \text{ cc O}_2(\text{SATP}) \text{ cm}^{-2} \text{ s}$ or $0.28 \text{ cc Air}(\text{SATP}) \text{ cm}^{-2} \text{ s}$ (SATP, standard ambient temperature, 25 °C, and pressure, 1 bar). SATP is assumed in the coming calculations. Adding methane

to air in the ratio $\text{CH}_4:\text{O}_2 = 1:2$ increases the required flow rate of the mixture to $0.31 \text{ cc(Gas) cm}^{-2}(\text{FC}) \text{ s}$, while adding hydrogen in the ratio $\text{H}_2:\text{O}_2 = 2:1$ increases the flow rate to $0.39 \text{ cc(Gas) cm}^{-2}(\text{FC}) \text{ s}$. Thus an average (and typical) value for the flow rate is

$$\frac{dV_0}{dt} = 0.35 \text{ cc(Gas) cm}^{-2}(\text{FC}) \text{ s} \quad (1a)$$

which corresponds to a gas velocity of

$$v = 0.35 \text{ cm s}^{-1} \quad (1b)$$

We use the notation cc(Gas) for one cc of the gas mixture and the notation $\text{cm}^2(\text{FC})$ for one cm^2 of the FC element.

In order to supply oxygen and fuel to all 100 elements (connected in series) the flow rate has to be a factor 100 higher. The gas velocity is thus $v = 35 \text{ cm s}^{-1}$. The (average) residence time for this configuration, τ_{res} , in the 0.4 cm stack is

$$\tau_{\text{res}} = 10 \text{ ms} \quad (2)$$

where it was assumed that the gas volume does not change in the reaction (as is the case in the reaction $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$). In view of our preliminary experience (see Section 4) a residence time of 10 ms seems to be adequately short.

The residence time is independent of the number of elements in the stack as the required gas velocity has to increase linearly with the number of elements. It is emphasized that this time is determined for maximum power and full fuel utilization. No fuel is meant to be wasted. When no current is drawn from the cell then no fuel and oxygen are consumed, provided the electrodes can be regarded as selective. Thus the flow rate should be decreased. If this increases the residence time beyond what can be tolerated then the reduction of the power output has to be achieved differently. This can be done by constructing the MR-SOFC in modular form, and shutting down part of the MR-SOFC modules while keeping others working at maximum power.

We are aware of one experiment done with a porous SOFC with the gas mixture flowing through the layers as required for this arrangement [31]. Only one element was constructed with the anode as the support. Unfortunately the problem of lack of selectivity came up and the gas flow had to be manipulated in order to generate significant power. (a) The gas composition was fuel rich with $\text{CH}_4:\text{O}_2 = 2:1$ and $1:1$ rather than $0.5:1$ as required for full oxidation. (b) The gas had to enter from the cathode side first (otherwise all the oxygen would have been consumed at the contact with the anode) and (c) the flow rate had to be kept high. The estimated residence time in the successful experiments should have been roughly $\sim 60 \text{ ms}$.

2.2. Supported SC-SOFC

Fig. 4 exhibits another configuration denoted as supported MR-FC (S-MR-FC). In this arrangement the cell element is supported on a dense substrate, the SE is again porous and so is, at least, the upper electrode. The gas mixture is supplied from one side only (upper side in Fig. 4) [37]. If the substrate cannot serve as an electrode then an electrode is added. This inner electrode

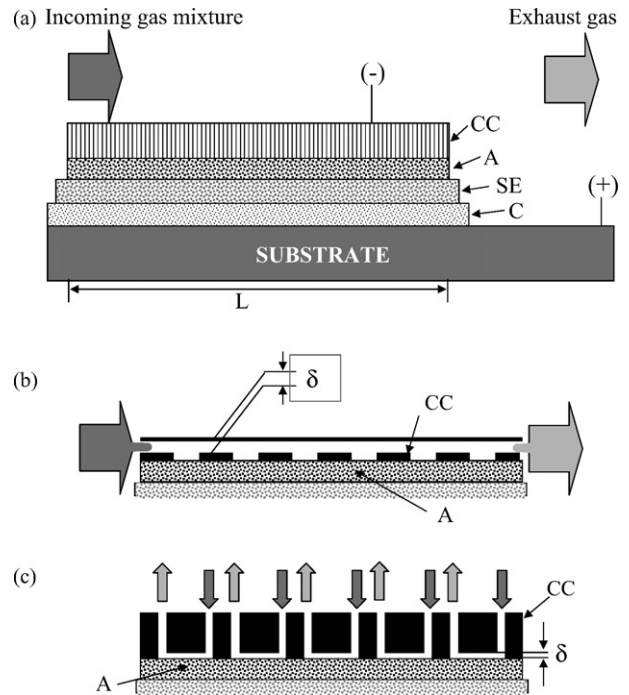


Fig. 4. S-MR-FC [37]. (a) The substrate is assumed to be conductive. The inner electrode is chosen as the cathode. (b) The gas is forced to flow in a narrow gap over the current collector in order to enhance the flow rate and reduce the residence time. (c) Another configuration of the CC that forces a different gas flow pattern.

can be dense (yet, a porous one is preferred as it has a higher active area). In Fig. 4(a) the inner electrode is chosen to be the cathode. On this electrode a porous SE is shown with a porous counter electrode on top of it (anode in Fig. 4(a)).

The residence time in this arrangement may be quite long unless special care is taken to shorten it, as is shown in the arrangements of Fig. 4(b) and (c). We now estimate this residence time. Let the length of the path for the gas flow be $L = 10 \text{ cm}$ and the width 1 cm . The volume demand for 10 cm^2 active area of the fuel cell is calculated from Eq. (1a) to be $dV/dt = L(dV_0/dt) = 3.5 \text{ cc(Gas) cm}^{-1}(\text{FC}) \text{ s}$ (where $\text{cm}(\text{FC})$ is 1 cm width of the FC). For the arrangement of Fig. 4(a) the residence time is not well defined as the volume (size and shape) beyond the current collector (CC) is not given. For the arrangement of Fig. 4(b) the gas velocity can be controlled by the gap thickness δ . Then $v = (dV/dt)/\delta$, and the residence time for this configuration is $\tau_{\text{res}} = L/v = \delta/(dV_0/dt)$ which with Eq. (1a) yields

$$\tau_{\text{res}} = \frac{\delta}{0.35 \text{ s}} \quad (3)$$

In order to reach 10 ms the gap δ has to be quite narrow, $\delta = 3 \mu\text{m}$, which would impose a high resistance to gas flow. We notice that the residence time is independent of L . However, the velocity is proportional to L and so is the impedance to gas flow. Thus a narrow FC with a low L value may be required. A more realistic gap is $\delta = 0.3 \text{ mm}$ which results in a rather long residence time of 1 s.

Fig. 4(c) is a modification which keeps the FC area high but the gas path length shorter. A closer look shows that the residence

time is not shorter for the same value of δ because, as we have seen before, the residence time does not depend on the length of the path L . However, the impedance to flow is expected to be lower for the shorter L value. On the other hand the more complex CC structure is expected to result in a high price.

We conclude that the residence time in the S-MR-FCs is expected to be longer than in the stack of Fig. 2. If a short residence times turns out to be a crucial parameter then the S-MR-FC is not a practical solution for a true MR-SOFC.

It turns out that all dense cells are subject to the same or very similar gas flow pattern and rate requirements. As a results all have the same typical residence time for the same value of the gap width δ . The residence time is most likely to be a few seconds if $\delta \sim 1$ mm in order to reduce the impedance to gas flow and if just the power output needs are met. It is the porous arrangement of Fig. 2 that allows the gas to flow through the cell layers which drastically reduces the residence time.

2.3. Side by side SC-SOFC

Fig. 5 exhibits an arrangement where the anode and cathode are applied to one side of the SE being exposed to the gas mixture. The SE is dense. The electrodes are in the form of stripes. The stripes can be connected in series or in parallel. This arrangement was first tested as a sensor [5] and later as a fuel cell [20,39,40]. Its performance was analyzed numerically [41,42]. (In the analysis of Calabrese Barton et al. [42] no interconnect is considered. However, adding an interconnect to the analysis should not alter the results dramatically.)

Unfortunately, this arrangement does not function well for two reasons. First, there is the problem of a long residence time typical of dense cells. Then, when power is generated, the inhomogeneous current density in the electrode becomes a problem. The current density at the edge of an electrode stripe is significantly higher than at the center [31,43]. The result is excess local heating of the edge of the electrode stripes resulting in chemical instability.

2.4. Planar, conventional design

The SC-SOFC mostly reported have a configuration that is the same as an element of a conventional SOFC (Fig. 1). The anode is applied on one side of the SE and the cathode on the opposite side. The solid electrolyte is usually dense. Experiments with a porous yttria stabilized zirconia (YSZ) SE but similar gas flow pattern (parallel to the layers rather than through them) show that the porosity leads only to a small decrease in power and open circuit voltage [28]. The decrease is probably due to some diffusion of the fuel intermediate products (H_2 and CO) from the

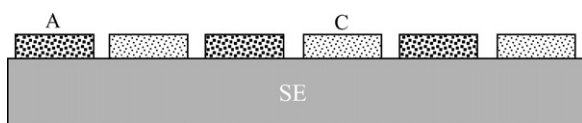


Fig. 5. Anode and cathode side-by-side SC-SOFC.

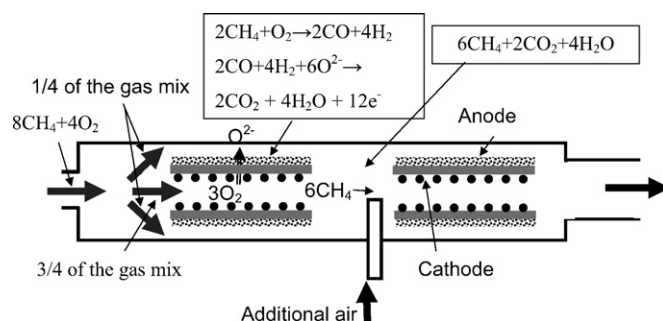


Fig. 6. Two SOFC elements in a SC-SOFC with a second stage used after injection of additional air [22]. Gas flow and reactions for methane as fuel.

anode, through the open pores of the $18 \mu\text{m}$ thick SE, towards the cathode and a lack of selectivity of the cathode.

Shao et al. have combined standard SOFC elements parallel in pairs and have suggested to connect them in series [21,22]. This is presented in Fig. 6. The materials used as electrodes are those used in SOFCs. The SE is Sm doped ceria and anode a mixture of the SE and Ni while the cathode is $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$. The operation temperature is 500 and 600 °C. The anode is known to be catalytic active and not possessing the required selectivity. The cathode exhibits selectivity under a high flow rate (short residence time). We analyze the performance of the SC-SOFC shown in Fig. 6 in order to demonstrate how, despite lack of selectivity, gas composition and flow pattern manipulation allows to operate successfully the cell in a single chamber.

A mixture rich with excess fuel is introduced. The excess in Fig. 6 is $\text{CH}_4:\text{O}_2 = 2:1$ which allows only partial reforming at the anode resulting in CO and H_2 . (One can also use a lower fuel concentration as long as full oxidation at the anode is not possible, e.g. $\text{CH}_4:\text{O}_2 = 1:1$.) The gas flow is carefully split so that $1/8$ flushes the anode of each element of the first pair and the remaining $3/4$ pass by the two cathodes of the first pair. Assuming that the cathode is selective (which holds approximately for a high flow rate, i.e. short residence time) the fuel there continues intact towards the exhaust of the first pair. The oxygen, on the other hand, is reduced at the cathodes to O^{2-} ions that flow through the electrolyte towards the anode and react there with the CO and H_2 to form CO_2 and H_2O . The overall reaction at the anode is (except for charge): $2\text{CH}_2 + 4\text{O}_2 \rightarrow 2\text{CO}_2 + 4\text{H}_2\text{O}$ where two O atoms come directly from the gas phase and six arrive in the form of ions through the SE. As $3/4$ of the fuel is exhausted unreacted the fuel utilization is 25% for a single stage (neglecting the potential energy loss in partial reforming). In order to increase the fuel utilization a second stage can be added to the cell provided additional air is also introduced to supply the missing oxygen for the second stage. Thus after two stages the fuel utilization can increase to $(1/4)(1 + 3/4) = 7/16 \sim 44\%$. Adding stages increases further the fuel utilization to $1 - (3/4)^n$ after n stages but it increase the cost of the device as well.

It should be noticed that this SC-SOFC functions well because the oxygen supply to the anode, at each stage, is limited and because the gas flow is controlled so that the gas streams flushing the anode and cathode are well separated.

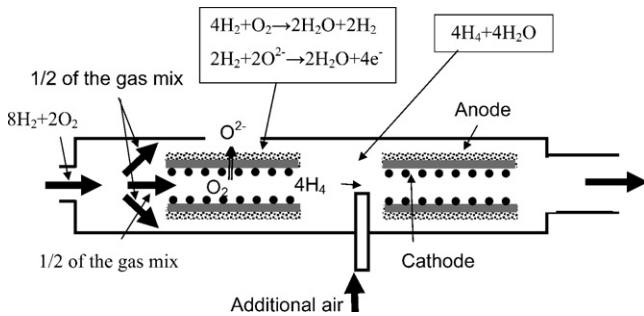


Fig. 7. Gas flow and reactions in a SC-SOFC of the design shown in Fig. 6 if hydrogen were used as fuel.

The same arrangement (with a selective cathode and non-selective anode) could function as a SC-SOFC with hydrogen as fuel provided hydrogen comes in excess and is sacrificed at the anode. This would eliminate the oxygen at the anode while leaving there excess fuel that allows the cell to operate. This is presented schematically in Fig. 7. The fuel utilization is 25% after the first stage with 25% of the fuel sacrificed. After the second stage it is $(1/4)(1 + 1/2)$ and after n stages, $(1/2)(1 - (1/2)^n)$. Here due to the non-selectivity of the anode, the fuel utilization is not only low but half of the fuel used is wasted as it is sacrificed to reduce the oxygen potential at the anode and it does not participate in the electrochemical reaction that generates the electrical energy.

2.5. Summary of the section of cell design

The most attractive design is that shown in Fig. 2. If realized its production will be simple and inexpensive and the power density high. It has, however, also the important advantage that it allows for the shortest residence time. The latter emerges as a possible crucial condition for achieving selectivity, as is discussed in Section 4.

3. Required catalytic properties of the different layers of a MR-SOFC

3.1. General

The selectivity normally looked for in heterogeneous catalysis is between different parallel chemical reactions. The selectivity one is looking for here is between electrochemical reactions and chemical ones. In the case of hydrogen as fuel this selectivity should be strict and no chemical reaction is tolerated. In the case of hydrocarbons as fuel, partial oxidation is tolerated but full oxidation is not and oxidation should be completed only via the electrochemical route.

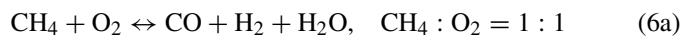
A selectivity between chemical and electrochemical reaction was already encountered in processes on Nafion [44]. There the electrochemical reaction is preferred to the chemical one. A selectivity between chemical and electrochemical reaction was also encountered in the NEMCA effect [45]. There, however, it is the chemical reaction that is preferred to the electrochemical one.

3.2. The overall reaction

The overall oxidation reaction is in the case of hydrogen as fuel:



The chemical reaction route is not tolerated in the MR-FC, of course. In the case of hydrocarbon the reaction can proceed in different ways. Let us examine methane as an example. However, methane may not be the best choice of an hydrocarbon for use in MR-SOFC due to its high chemical stability [46]. The following chemical reactions are a priori possible in the full and partial oxidation of methane [29]:



The presence of water results in a water gas shift reaction [47]:



and also in steam reforming:



CO_2 reforming is also possible [47,48]:



and of course full oxidation:

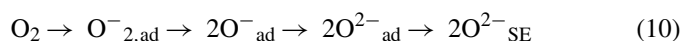


Reactions leading to carbon deposition are not considered as in the presence of a high concentration of oxygen, as should be used in MR-SOFC, they are not expected to take place.

We notice that in MR-SOFC only one chemical reaction is totally unacceptable. This is the last one, Eq. (9). It results in full oxidation. All other reactions result in partial oxidation and leave some fuel for operating the cell. Unfortunately, this partial reforming wastes some of the free energy of the reaction that could be converted into electrical energy. However, at this stage of the R&D this is a minor consideration as one is striving to a proof of principle of a true MR-SOFC and could tolerate some losses.

3.3. The reaction at the cathode

The cathode task in an SOFC depends on the nature of the SE. In the case the SE conducts oxygen ions, e.g. YSZ, the cathode has only to reduce the oxygen molecule to oxygen ions which then enter the SE. If the SE conducts protons then the cathode has to handle also the reaction of the protons with oxygen. We consider here the first case, of an oxygen ion conducting SE. The reduction of oxygen at the cathode may involve various steps, such as



where the second to fourth specie are adsorbed (ad) ones and the last denoted an oxygen ion in the SE.

In a MR-SOFC the cathode is exposed also to the fuel. In the case of hydrogen as fuel the cathode should not act as a catalyst for the reaction of Eq. (4). For the catalytic process it is most likely that an adsorbed specie of hydrogen is the active specie that reacts with the adsorbed oxygen specie. Therefore a proper cathode will, most probably, be found among those materials that do not adsorb hydrogen.

When the fuel is methane the cathode should be looked for among materials that do not adsorb methane or the fuel products, CO and H₂, of partial oxidation reaction.

In the case the reaction on the cathode occurs only between adsorbed and charged species, adsorption of neutral fuel specie can be tolerated but not of charged ones. Then one would look for a material that donates electrons to the adsorbed oxygen, while being unable to accept an electron from the adsorbed fuel, i.e. has a low work function. The cathode can be a metal, semiconductor or a mixed ionic electronic conductor (MIEC). It need not be n-type as long as the adsorbed oxygen acceptor level is close or below the Fermi level of the cathode.

3.4. The reaction at the anode

The reaction at the anode is expected to occur between the fuel and the oxygen ion emerging from the SE. The latter can go through a series of steps, e.g. the inverse of that in Eq. (10). It is most likely that the fuel oxidation reaction occurs between an adsorbed specie of the fuel, say H⁺, and mainly one of those oxygen specie emerging from the SE. For example



Thus one should look for an anode among those materials that do not adsorb oxygen from the gas phase. The oxygen specie emerging from the SE may have a different reaction rate with the fuel than the oxygen in the gas phase. An indication for this is a difference in the activity of oxygen ions emerging from the SE and spilled over an electrode from those ions adsorbed from the gas phase onto the same electrode. This is observed at relatively low temperatures in the NEMCA effect [45,49] but also at elevated *T* where oxygen supplied via the SE to an YBa₂Cu₃O_{*x*} (YBCO) electrode oxidizes methane to CO while oxygen supplied from the gas phase yields CO₂ in the presence of YBCO [50]. (Unfortunately, in the last two examples oxygen from the gas phase reacts more strongly with the fuel than the oxygen emerging from the SE.)

In the case the reaction on the anode occurs only between adsorbed, charged species, one would look for a material that accepts electrons, i.e. has a high work function and is not likely to reduce oxygen from the gas phase.

Comparing the requirement for the anode (electron acceptor) and cathode (electron donor) with the successful electrode materials for SOFCs one may wonder if the former theoretical claims and the practice are not in contradiction. In SOFCs the anode including the nearby SE are reduced, raising the Fermi level there. Yet it is found that this reduction enhances the anode

reaction, e.g. when CeO₂ is used. In the same sense, oxidation at the cathode lowers the Fermi level but enhances the electrode reaction. This suggests that the electrode reactions enhancement is due to the change of stoichiometry in the SE rather than a desired change in the work function. The stoichiometry change enhances the electron/hole concentration and the electronic (electron/hole) conductivity in the SE, which otherwise is an insulator with respects to the electronic current. This facilitates the widening of the triple phase boundary (tpb). Thus the active electrode area is increased [51]. The stoichiometry change in the SE is not required when the electrode is an MIEC as the latter acts as a wide tpb. This suggests that the proper selective electrode material is a highly electron/hole and ion conductive MIEC which also possesses the correct work function.

It should be noticed that an MIEC can be replaced by a quasi-MIEC which consist of a mixture of finely dispersed two phases, one conducting electrons or holes and the other ions.

3.5. The required inertness of the SE and ICN

A simple requirement for the SE and ICN would be that they are inert with respect to both the chemical oxidation reaction and the electrochemical ones. Their task is different from that of the electrodes. They need not catalyze any reaction. However, this is not a necessary condition and imposing it may, eventually, introduce a limitation on the choice of materials. Let us therefore examine to what extent this limitation can be relaxed.

The SE and ICN should definitely, as the electrodes, exhibit no catalytic activity towards the chemical oxidation reaction if the fuel is pure hydrogen. When a hydrocarbon fuel is used one could tolerate partial oxidation under the following conditions, that the other layers in the MR-SOFC do not further catalyze the full oxidation of the products of that partial oxidation.

As to the electrochemical reactions the SE and ICN could be either inert or be allowed to exhibit the same catalytic activity as the *adjacent* electrode. It is, of course, not tolerated that the SE or the ICN catalyzes the same electrochemical reaction on both sides. The catalytic properties may be different on the two sides of the same material (SE, ICN) if the catalytic process includes steps both on the SE or ICN and on the nearby electrode. Would this situation arise in reality? Perhaps, and attention to that possibility should be paid.

As mentioned before diffusion of electro-active specie through the pores of the ICN should be negligible.

3.6. Parameters that control or allow selectivity

Priestnall et al. [36] review, among others, mechanisms for breaking the symmetry: (a) selectivity of the electrode material, (b) diffusion selectivity, (c) differential flow rates, and (d) selectivity by adding a diffusion filter layer on top of the electrode, e.g. fuel permeable, oxygen impermeable barrier. To that one has to add three important parameters: (a) temperature, (b) residence time and (c) fuel to oxygen ratio in the gas mixture. One has also to remember that the outcome can be a mixed potential due to competing reactions. Many of these factors seem to con-

tribute to the selectivity of the electrode pairs tested in supported MR-FCs [37].

3.6.1. Temperature

The temperature has a significant effect on the catalytic rates and on the selectivity. In general reducing the temperature slows down reaction rates. Indeed, a true MR-FC was found to date only at close to room temperature. Calabrese Barton et al. [42] report on selectivity in the bipolar cell: cathode – FeTMPP (iron tetramethoxyphenyl porphyrin), anode – Pt–Ru and SE – Nafion® 117 (fed with a mixture of methanol and air).

In order to demonstrate the effect of temperature on selectivity let us consider the example of the NEMCA effect, though there the preferred reaction is the chemical one rather than the electrochemical one. In the NEMCA experiments a gas, say methane, is mixed with oxygen and oxidized on a catalyst. The latter is part of a Galvani cell that can transfer oxygen from a fixed oxygen reservoir (air) through a SE (YSZ) to the catalyst electrode. It turns out that at relatively low temperatures ($\sim 450^\circ\text{C}$) the oxygen ions that emerge from the SE do not participate in the oxidation reaction. Oxidation occurs almost entirely by the oxygen coming from the gas phase. On the other hand, at higher temperatures $T > 600^\circ\text{C}$ oxygen pumped through the Galvani cell does participate in the reaction. The reason for that peculiar behavior at the lower temperatures is a potential barrier that blocks the oxygen ions emerging from the SE from being transferred into a specie that can quickly react with methane [45]. At elevated temperatures ($T > 600^\circ\text{C}$) this potential barrier is easily crossed and the methane oxidation by oxygen ions supplied via the SE may take place [50].

We tentatively assume that the operating temperature of a MR-SOFC will be about 600°C perhaps in the $500\text{--}600^\circ\text{C}$ range. This upper temperature limit is based on the result of catalysis measurements reported in Section 4 below, while the lower limit results from the knowledge that the reaction rates are too low below $\sim 500^\circ\text{C}$. These limits may, however, change as the applicability of new materials is discovered.

3.6.2. Residence time

The residence time is the time a molecule is present in the reaction zone, which, in the present case, is the stack of the ceramic layers. The electrodes serve as catalysts. As heterogeneous catalysis has to start with adsorption on the catalyst the probability of adsorption of a molecule is proportional to the time spent near the electrode material. Adsorption may be followed by fast desorption or the active species in the desired reaction may not be the first adsorbed specie but rather one obtained by dissociating the molecule and perhaps charging (see Eq. (10) as an example). However, it is clear that shortening the residence time sufficiently must eventually reduce the reaction rate. Unfortunately, this may reduce both the chemical reaction rate and the electrochemical reaction rate. Thus taking advantage of a short residence time can be achieved only for reactions understood in detail and then properly selected. We shall demonstrate below that if only the chemical reaction is examined its rate is decreased as the residence time is shortened, as required.

3.6.3. Fuel to oxygen ratio in the gas mixture

This ratio determines whether the mixture is oxidizing or reducing. Thus, depending on that ratio the gas mixture may affect differently the stoichiometry of the materials used and their catalytic activity.

3.6.4. Materials

The properties of the four materials involved in the stack (anode, cathode, SE and ICN) were discussed before. Results of a screening test are reported in Section 4.

The products of reaction have also to be taken into consideration for the following reasons:

- Adsorption of a product, e.g. water, onto the cell materials may change their catalytic properties.
- The products may participate in the reaction by changing the concentration ratio between the product components and the reactant. This may require changes in the electrode material along the gas stream in order to maintain selectivity.
- In the case of hydrocarbon the product may shift the reaction to other routes such as steam reforming or CO_2 reforming of methane. This may require changes in the electrode composition along the gas stream in order to maintain selectivity.
- The dilution of the reactant down stream reduces the danger of explosion.

3.6.5. Diffusion selectivity and differential flow rates

These processes, if effective, can usually be taken advantage of in a certain range of gas flows and pressure distributions. Thus for a continuous operation the gas flow needs to be kept constant. This implies that the FC has to operate under constant conditions. Thus changes in the FC power output should only be done by switching on and off part of the MR-SOFC modules while keeping the others operating under standard conditions.

3.6.6. Filter layer on top of the electrode

A layer applied onto the electrode may serve as a filter for the oxygen or the fuel. A typical example is Pd, which can filter hydrogen. Unfortunately, the catalytic activity of this layer may have an adverse effect on the MR-SOFC operation. This would be the case with Pd which catalyses the chemical oxidation of methane [52]. In addition, the products have to diffuse through that layer if applied onto an anode when the SE conducts oxygen ions (or on the cathode when protons are conducted). Thus adding a filter layer requires careful examination of the overall effect of that solution.

3.7. Methods for testing selectivity in MR-SOFCs

Various procedures were used for testing the selectivity of certain materials as anode or as cathodes. The basic one is to measure the voltage and power output of a SC-SOFC element. However, the interpretation is not unique and this cannot be used as a stand alone method. A further extension was presented by Hibino et al. [40,53] where the two electrode compartments are separated and the reaction products at the tested electrode are analyzed. When the SE conducts oxygen ions the product

of the electrochemical reaction should be looked for on the anode side. What is of interest is the rate these products are formed compared to the current through the cell. If the electrodes are selective the current is directly related to the rate of fuel consumption. If excess fuel is consumed this indicates parasitic reaction and non-selectivity. The ratio between the current generated and the rate of fuel consumption can be used to quantify the selectivity of the electrodes used (under the operating conditions).

Calabrese Barton et al. [42] improved this analysis by adding another test procedure. The separated anode is first supplied with fuel (aqueous methanol) only (while the cathode is flushed with air) and the cell current is measured. In addition the products are analyzed (for CO₂ production). Then with the same fuel supply rate, air or (at the same gas supply rate) pure nitrogen is added to the fuel. At low current densities no difference is observed in the cell current and CO₂ production rate for the three cases. This indicates that the anode tested (Ru–Pt at 80 °C) is selective. Under high current density the last two cases, with air or nitrogen added, show the same but higher impedance than the pure fuel case. Yet the current–CO₂ ratio indicates no parasitic oxidation of methane by oxygen from the gas phase which would yield CO₂ but no contribution to the current. The increase in the impedance can thus be identified as mass transport limitation of the fuel in the presence of the extra gases (air or nitrogen).

A straight forward, but partial, characterization method is to measure the catalytic activity of the electrode material (as well as two phase mixtures) towards the direct chemical reaction. It provides an answer for one necessary condition, namely does the material catalyze the chemical oxidation reaction of the fuel. It thus can only be used for screening (see Section 4). It has to be supplemented by positive results of catalyzing the electrochemical reaction.

Napporn et al. [24] have embedded the test cell in a blanket of flowing nitrogen while the cell is held by rather tight current collectors that force the gas stream to go in one direction only. In this way (when the two flow rates are high enough and the amount of gas diffusing up stream can be neglected) the exhaust gas from the cathode side cannot flow back into the anode side and vice versa. The latter back diffusion, if allowed, adversely affects the results, in particular, the identification of the process products at each electrode. In another publication [23] they use the temperature after the SOFC element as a measure for the selectivity of the electrode. No calibration is provided relating the temperature increase to lack of selectivity. The presence of both Pt and Ni results in a temperature increase. However, that in the presence of Pt is significantly higher than when Ni is included in the anode.

4. Experimental results of the catalytic activity of materials towards the chemical oxidation of methane

We report here on screening experiments of materials, most of them commonly used in SOFC. The experiment examines the catalytic properties of the materials towards the direct chemical reaction. Those which fail this test can certainly not be used in

an MR-SOFC. The experimental system consists of a reactor in the form of a 4 mm inner diameter, and long quartz tube which contains lightly pressed powder of the material under test. Two pieces of alumina wool are used as stoppers to keep the powder in place. The powder forms a small cylinder ~10 mm long and 4 mm diameter. The stopper down stream is held in place by a long alumina tube, 2 mm wide. This is done in order to allow the use of enhanced pressures (up to 2.5 atm) to generate higher flow rates and reduced residence times. (Safety measures are taken for the case of explosion of the tube.) A gas chromatograph, GC, is used to analyze the incoming and out going gas. Parameters changed for each material are (a) temperature (500–700 °C), (b) gas composition (fuel rich and fuel lean) and (c) gas flow rate, expressed in terms of the residence time in the 10 mm long active zone of the reactor (i.e. contains the tested material, subject to a uniform temperature). The empty reactor did not catalyze the reaction at temperatures below 850 °C. The results are summarized in Table 1. The accuracy is ±5% absolute value.

The data in Table 1 show the following:

- (a) Out of the materials tested ITO and silver are inert up to 700 °C. CuO, at 700 °C exhibits strong dependence on τ_{res} and weak activity under a short residence time of 75 ms suggesting that it can be considered inert for a residence time of 10 ms. Ta₂O₅ is inert at 600 °C and weakly active at 700 °C for a residence time of 150 ms.
- (b) Change of stoichiometry of an oxide changes activity. The materials that exhibits limited activity under oxidizing conditions are: SSCO at 500 °C and ZnO up to 600 °C while being enhanced under reducing conditions.
- (c) Due to reduction, hysteresis is observed when using YSZ after cooling to 500 °C under reducing conditions. Significantly enhanced catalytic activity is observed, as compared to oxidized YSZ, when the gas composition is switched back to a lean one. Recovery time at 500 °C is much longer than 10 min. At this temperature oxygen uptake is expected to be slow. Thus the catalytic activity in the reduced YSZ should not be associated with oxygen storage and release but rather with an enhanced electronic (electron) charge carrier concentration and/or high Fermi level and thus smaller work function.
- (d) Ni turns out to be rather weakly active, under lean conditions, at 600 °C for a residence time of 75 ms. This suggests that it might be inert for $\tau_{\text{res}} = 10$ ms.
- (e) YSZ is found to be quite active at 600 °C and only inert at 500 °C for $\tau_{\text{res}} = 150$ ms. Shortening τ_{res} to 75 ms reduced the activity significantly indicating that under 10 ms YSZ could probably be used at 600 °C.
- (f) SDC is quite active even at 500 °C at $\tau_{\text{res}} = 150$ ms.
- (g) Two materials exhibit excessive activity. BCYO (BaCe_{0.9}Y_{0.1}O_{3- δ}) is very active at 600 °C but changed abruptly at 500 °C to an inert material for a rather short residence time of 25 ms. Nd₂O₃ is active down to 500 °C.
- (h) LSM tested at 650 °C was reduced by methane though the gas mixture was somewhat lean.

Table 1
Percentage^a of deficient reactant consumed by chemical oxidation^b

	Material	O ₂ :CH ₄ :N ₂ ¹	τ_{res} (Sec)	500°C	600°C	700°C
1	Ag	L=2.1:1:8	0.38 ²	————	————	$\Delta\text{CH}_4 = 0$
2	BCYO	R=2.1:1:8	0.025 ³	0 at 535°C	$\Delta\text{CH}_4 = -100$	$\Delta\text{CH}_4 = -100$
3	CuO	L=3:1:10	0.15	$\Delta\text{CH}_4 = -20$	$\Delta\text{CH}_4 = -50$	$\Delta\text{CH}_4 = -55$
		L=2.1:1:8	0.075	————	$\Delta\text{O}_2 = -5$	$\Delta\text{O}_2 = -5$
4	ITO	L=3:1:10	0.15	0	————	0
		R=1:1:4	0.15	0	————	0
5	LSM	L=2.1:1:8	0.075	CH ₄ reacts with LSM ($\Delta\text{O}_2=0$) at 650°C. ⁴		
6	Nd ₂ O ₃	L=3:1:10	0.15	$\Delta\text{CH}_4 = -50$	$\Delta\text{CH}_4 = -75$	$\Delta\text{CH}_4 = -90$
7	Ni	L=2.1:1:8	0.075	————	$\Delta\text{O}_2 = -20$ at 570°C	$\Delta\text{O}_2 = -50$ At 670°C
8	SDC	L=3:1:12	0.15	$\Delta\text{CH}_4 = -95$	$\Delta\text{CH}_4 = -100$	$\Delta\text{CH}_4 = -100$
		L=2.1:1:8	0.025 ³	————	$\Delta\text{O}_2 = -50$	————
		R=1:1:4	0.15	$\Delta\text{O}_2 = -100$	————	$\Delta\text{O}_2 = -100$
9	SSCO	L=3:1:10	0.15	$\Delta\text{CH}_4 = -5$	$\Delta\text{CH}_4 = -55$	$\Delta\text{CH}_4 = -80$
		R=1:2:8	0.15	$\Delta\text{O}_2 = -25$	$\Delta\text{O}_2 = -85$	$\Delta\text{O}_2 = -100$
10	Ta ₂ O ₅	L=3:1:10	0.15	0	0	$\Delta\text{CH}_4 = -25$
		R=1:1:3.4	0.15	0	$\Delta\text{O}_2 = -10$	$\Delta\text{O}_2 = -10$
11	YSZ	L=2.1:1:8	0.075	————	$\Delta\text{O}_2 = -10$	$\Delta\text{O}_2 = -55$
		L=3:1:12 ⁵	0.15	0	$\Delta\text{CH}_4 = -35$	$\Delta\text{CH}_4 = -70$
		R=1:1:4 ⁵	0.15	0	$\Delta\text{O}_2 = -10$	$\Delta\text{O}_2 = -65$
12	ZnO	L=3:1:10	0.15	0	$\Delta\text{CH}_4 = -5$	$\Delta\text{CH}_4 = -20$
		R=1:2:8	0.15	$\Delta\text{O}_2 = -10$	$\Delta\text{O}_2 = -30$	$\Delta\text{O}_2 = -75$
	Empty ⁶	L=3:1:10	0.38 ²	————	————	$\Delta\text{O}_2 = -5$ at 800°C
		R=1:1:4	0.38 ²	————	————	$\Delta\text{O}_2 = -5$ at 800°C

¹R, rich in fuel, L, lean in fuel. ²Notice extended τ_{res} . ³Notice short τ_{res} . ⁴No oxygen from the gas phase is consumed in the rapid oxidation of methane, rather than coming from LSM. ⁵Hysteresis was observed after cooling from 700 to 500 °C under reducing atmosphere. When at 500 °C the gas was switched back to L = 3:1:12 and a measurement taken within 10 min. The methane concentration change in the reactor was -40%, indicating that the YSZ is still reduced and more active. ⁶Empty reactor: quartz tube. Gray background: high catalytic activity. The chemical reaction results in a concentration change beyond 50% (at the given residence time).

^a Accuracy: $\pm 5\%$.

^b Full oxidation of that part of the fuel that has reacted. The products detected were mainly H₂O and CO₂, and not those of partial reforming: CO and H₂.

These results lead to the following conclusions:

- There are few materials that are strictly inert, however others can be found that, by reducing the residence time and/or temperature, can be considered inactive towards the catalysis of the oxidation of methane.
- Since the estimated residence time in an MR-SOFC is 10 ms it is anticipated that there will be sufficient materials that can be applied.
- The results suggest that the operation temperature of an MR-SOFC will have to be limited by 600 °C.
- The solid electrolyte will most probably be YSZ, or one of those that were not tested yet, e.g. La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}. SDC can be considered only at

lower temperatures because of its high catalytic activity.

- At relative low temperatures, ≤ 600 °C, other materials, not only oxides, can be considered for use as electrodes. This opens the field to nitrides, carbides and metallic alloys.

When hydrogen is used as the fuel, high temperatures can still be used. Contrary to common belief hydrogen can coexist with oxygen at elevated temperatures in an inert surrounding. Supported MR-SOFCs [37] exposed to such gas mixtures exhibited finite cell EMF at 650 °C. Partial reforming of hydrocarbons in the presence of excess oxygen should also lead to a gas mixture containing hydrogen (and CO) and oxygen. This and the

simplicity of the hydrogen oxidation process as compared to the methane oxidation one, suggests to continue the research on MR-SOFC, in the near future, using hydrogen as fuel rather than methane.

5. Flow rate impact on the performance of SC-SOFC

It has been reported that the flow rate of the gas mixture has a significant impact on the open circuit voltage as well as on the power output in SC-SOFCs. Hibino et al. [40] show that in a SC-SOFC as shown in Fig. 1, for a gas mixture $\text{CH}_2:\text{O}_2 = 1:1$, under a flow of 50 ml min^{-1} , over a cell $\text{Ni} + \text{GDC}|\text{YSZ}|\text{LSM} + \text{MnO}_2$, electrolyte supported, the EMF is almost zero. The EMF increases with flow rate and reaches a plateau of 800 mV, at 200 ml min^{-1} . On the other hand, for the gas composition $\text{CH}_4:\text{O}_2 = 1:2$ (which would allow full oxidation) the EMF vanishes even at a higher flow rate of 300 ml min^{-1} . The last result can be understood to be due to lack of selectivity of the Ni + GDC anode.

Though a single chamber is used, it is clear that the gas flushing the anode continues to the exhaust line and does not reach the cathode. Thus the cell can function even if the anode is not selective as long as the gas mixture is fuel rich ($\text{CH}_4:\text{O}_2 = 1:1$) and the cathode is selective. The fact that the EMF vanishes for a flow rate of 50 ml min^{-1} indicates that the cathode is not selective either. Once the flow rate increases and the residence time decreased, the cathode becomes selective which results in a finite EMF.

Similar results were reported by Buegler et al. [30,31] on cells based on GDC as electrolyte. Additional tests demonstrate the different catalytic activity of the anode and cathode used [31, Chapter 5]. One of the cell considered is (Ni + GDC|GDC|SSCO). It is fed with a mixture of air and methane with $\text{CH}_4:\text{O}_2 = 2, 1.5$ or 1. The anode and cathode compartments are separated, but the two electrodes are flushed by the same gas mixture. It is shown that the cathode and anode materials both catalyze the chemical reaction though the anode material is more active.

Buegler et al. report on the first porous SC-SOFC with flow through of the gas mixture [31, Chapter 9]. The porous cell Ni – GDC|GDC|SSCO is anode supported, the cathode and electrolyte 20–30 μm thick. The cathode has a Pt mesh embedded as a current collector while at the anode the Pt mesh is pressed onto it. The gas mixture is entering through the cathode. Gas mixture contains methane, air and $\sim 3\%$ H_2O . The results are quite similar to the ones reported for the dense electrolyte supported cell. The EMF and power density increase with flow rate. At 1000 ml min^{-1} yet no maximum in the EMF and power density versus flow rate, is reached. These results can again be interpreted by a non-selectivity of the anode and a selectivity of the cathode that increases with the flow rate and decreases in the residence time.

The effect of flow rate was attributed by others to a possible back flow of the gas flushing the cathode, going towards the anode and reacting there and that this back flow is reduced as the flow rate increases. This cannot explain the flow rate dependence observed also in tests using two compartments.

One of the reasons for the low utilization is due to the high flow rate used, with a lot of fuel remaining unused. The second reason is the need to use fuel rich gas mixtures and the sacrificing of some fuel due to the non-selectivity of the anode.

6. Conclusions

It has been shown that SOFC which really can operate on a gas mixture of fuel and air, denoted here as MR-SOFC, have significant technological advantage over common SOFC. Further, it was argued that all single chamber SOFC (SC-SOFC) considered to date do not fulfill this requirement due to lack of selectivity of the anode and limited selectivity of the cathode (that sets in only under short residence time). The fact that power is generated in the SC-SOFC is not because of selectivity of the electrodes but rather due to (a) gas composition and (b) flow pattern manipulation that renders the SC-SOFC to function as common SOFCs with excess fuel remaining at the anode. The control of the residence time is an acceptable means for improving selectivity, however, the first two parameter manipulations (a) and (b) cannot be tolerated in a multi stack arrangement, as shown in Fig. 2.

The most promising cell design, to date, is that shown in Fig. 2. It is interesting due to its simplicity and expected low fabrication price, high power density and high fuel utilization. The design allows also for a low residence time. This property may turn out to be a crucial property for finding selective electrodes as well as inert SEs and ICNs.

Attention has to be paid to the design of the porosity in order to minimize the back pressure needed to drive the gas mixture while keeping a large contact area between the gas and the cell materials. The latter requires that the contact area is high which can be achieved using many fine pores. The former requires that the pores are large. Therefore the optimal design needs to be a combination of both types of pores in communication.

Explosion risk in MR-SOFCs may exist. However, the porous cell (of Fig. 2) will serve as a heat sink reducing the possibility of a rapid reaction and explosion. The gas mixture can be further diluted. It is self-diluted by the products of the process down stream. On top of this the MR-SOFC has to be maintained in a robust container.

The selectivity one is interested in is of special nature, favoring electrochemical reactions to chemical ones. Unfortunately, little was done so far in this direction. Till now the efforts in SC-SOFC research were concentrated, mainly, on ceramic processing of the layers and construction of SOFC elements.

While shortening the residence time seems to improve selectivity and thus MR-SOFC performance, one has to bear in mind that it may have an adverse effect on the electrochemical reactions needed. Both effects have to be examined.

The reaction products affect the reaction. In particular, in the case of methane the reaction products, water and carbon dioxide, may participate in the reaction down stream in the cell of Fig. 2. They may also be adsorbed onto the cell layers changing their catalytic properties. Thus the composition of the cell layers may have to change going down stream in order to adjust their catalytic properties to the gas composition. If this is indeed so,

then one may run into the need to keep the gas composition distribution constant in time. This means that the power output of a module should be kept constant in time. In that case changing the over all power output of a device can be achieved only by switching off/on of modules which, when “on”, work under fixed conditions.

Future research should, first of all, concentrate on the possible mechanisms and materials with the suitable selectivity. The temperature that allows selectivity appears to be limited by 600 °C. This opens new possibilities to look for materials not only among the oxides. These materials can be looked for under nitrides, carbides and elemental metals and their alloys. The suitable electrode material will operate at $T \leq 600$ °C under a mixture of air and fuel, reach a steady state surface composition and provide the necessary selective catalytic properties. The suitable solid electrolyte and interconnect would exhibit inertness or selectivity.

Key parameters to be varied in search for the suitable selectivity are:

- (a) Materials for each of the four layers (anode, cathode, SE and ICN).
- (b) Combinations of materials for contacting layers (possible catalytic processes which rely on two phases).
- (c) Fuel type.
- (d) Fuel, air and exhaust gas ratio.
- (e) Diluting agents.
- (f) Gas mixture flow rate.
- (g) Residence time.
- (h) Temperature.
- (i) Layer porosity and structure.
- (j) Electrical current density.

The value of the gas flow rate is of little meaning. It is the residence time in the reactive zone, being fixed by the flow rate, which should be reported.

Acknowledgements

This research was supported by the Ministry of Infrastructure. The author thanks Sergey Yusimov for preparing the multi layer ceramic stack and for performing the GC measurements and Meir Behar for many helpful discussions.

References

- [1] C. Eyroud, J. Lenoir, M. Gèry, C. R. Acad. Sci. Paris 252 (1961) 1599.
- [2] G. Grüneberg, W. Wicke, E. Justi, British Patent 994448 (1961), French Patent FR 1321373.
- [3] W. van Gool, Philips Res. Rep. 20 (1965) 81.
- [4] G. Goebel, B.D. Struck, W. Vielstich, in: W. Vielstich (Ed.), Fuel Cells—Modern Processes for the Electrochemical Production of Energy (English translation by G.J.G. Ives), Wiley/Interscience, NY, 1965, pp. 374–376.
- [5] N. Miura, H. Kato, N. Yamazoe, T. Seiyama, Proceedings of the 1st International Meeting on Chemical Sensors, Fukuoka, 1983, p. 233.
- [6] C.K. Dyer, US Patent 4863813 (1988/1989).
- [7] C.K. Dyer, Nature 343 (1990) 547.
- [8] C.K. Dyer, US Patent 5094928 (1990/1992).
- [9] C.K. Dyer, US Patent 4988582 (1990/1992).
- [10] P. Mosely, D. Williams, Nature 346 (1990) 23.
- [11] S. Gottesfeld, Nature 345 (1990) 673.
- [12] G.A. Louis, J.M. Lee, D.L. Maricle, J.C. Trocciola, US Patent 4248941 (1981).
- [13] T.E. Mallouk, Nature 343 (1990) 515.
- [14] P.C. Ellegen, US Patent 5162166 (1991/1992).
- [15] T.M. Taylor, US Patent 5102750 (1990/1992).
- [16] T. Hibino, H. Iwahara, Chem. Lett. 22 (1993) 1131.
- [17] I. Riess, P.J. van der Put, J. Schoonman, Solid State Ionics 82 (1995) 1.
- [18] T. Hibino, K. Asano, H. Iwahara, Chem. Lett. (Jpn.) 23 (1994) 485.
- [19] T. Hibino, H. Tsunekawa, S. Tanimoto, M. Sano, J. Electrochem. Soc. 147 (2000) 1338.
- [20] T. Hibino, A. Hashimoto, M. Suzuki, M. Yano, S. Yoshida, M. Sano, J. Electrochem. Soc. 149 (2002) A195.
- [21] Z. Shao, S.M. Haile, Nature 431 (2004) 170.
- [22] Z. Shao, S.M. Haile, J. Ahn, P.D. Ronney, Z. Zhan, S.A. Barnett, Nature 435 (2005) 795.
- [23] T.W. Napporn, F. Morin, M. Meunier, Electrochem. Solid State Lett. 7 (2004) A60.
- [24] T.W. Napporn, X. Jacques-Bédard, F. Morin, M. Meunier, J. Electrochem. Soc. 151 (2004) A2088.
- [25] X. Jacques-Bédard, T.W. Napporn, R. Roberge, M. Meunier, J. Power Sources 153 (2006) 108.
- [26] I.C. Steffan, C.P. Jacobson, S. Visco, L.C. de Jonghe, Electrochem. Solid State Lett. 7 (2004) A198.
- [27] T. Suzuki, P. Jasinski, H.U. Anderson, F. Dogan, Electrochem. Solid State Lett. 7 (2004) A391.
- [28] T. Suzuki, P. Jasinski, V. Petrovsky, H.U. Anderson, F. Dogan, J. Electrochem. Soc. 152 (2004) A527.
- [29] B.E. Buegler, A.N. Grundy, L.J. Gauckler, J. Electrochem. Soc. 153 (2006) A1378.
- [30] B.E. Buegler, M.E. Siegrist, L.J. Gauckler, Solid State Ionics 176 (2005) 1717.
- [31] B.E. Buegler, PhD Thesis, Department Materials ETH Zürich, 2006.
- [32] M. Yano, A. Tomita, M. Sano, T. Hibino, Solid State Ionics 177 (2007) 3351.
- [33] I. Riess, Solid State Ionics 176 (2005) 1667.
- [34] I. Riess, Solid State Ionics 177 (2006) 1591.
- [35] M.A. Priestnall, M.J. Evans, M.S.P. Shaffer, Patent PCT No. WO 01/73881 A1, October 4, 2001.
- [36] M.A. Priestnall, V.P. Kotzeva, D.J. Fish, E.M. Nilsson, J. Power Sources 106 (2002) 21.
- [37] S. Raz, M.J.G. Jak, L.N. van Rij, J. Schoonman, I. Riess, Solid State Ionics 149 (2002) 335.
- [38] I. Riess, M. Gödickemeier, L.J. Gauckler, Solid State Ionics 90 (1996) 91.
- [39] M. Gödickemeier, D. Nussbaum, C. Kleinlogel, L.J. Gauckler, Proceedings of the Joint International, 192nd Meeting of Electrochemical Society, 48th Meeting International Society of Electrochemistry, Paris, France, August 31–September 9, 1997, Abstract No. 2191.
- [40] T. Hibino, S. Wang, S. Kakimoto, M. Sano, Solid State Ionics 127 (2000) 89.
- [41] J. Fleig, H.L. Tuller, J. Maier, Solid State Ionics 174 (2004) 261.
- [42] S. Calabrese Barton, T. Patterson, E. Wang, T.F. Fuller, A.C. West, J. Power Sources 96 (2001) 329.
- [43] B.E. Buegler, M. Ochsner, S. Vuillemin, L.J. Gauckler, J. Power Source 171 (2007) 310.
- [44] M.J.G. Jak, S. Raz, L.N. van Rij, J. Schoonman, I. Riess, Solid State Ionics 143 (2001) 205.
- [45] I. Riess, C. Vayenas, Solid State Ionics 159 (2003) 313.
- [46] M. Mogensen, K. Kammer, Annu. Rev. Mater. Res. 33 (2003) 321.
- [47] K. Kockloefel, in: G. Ertl, K. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, vol. 4, Wiley-VCH, pp. 1819–1824.
- [48] Y.H. Hu, E. Ruckenstein, Adv. Catal. 48 (2004) 297.

- [49] C.G. Vayenas, S. Bebelis, I.V. Yentekakis, S. Neophytides, in: P.J. Gellings, H.J.M. Bouwmeester (Eds.), *CRC Handbook of Solid State Electrochemistry*, CRC Press Inc., 1997, pp. 445–480 (Chapter 13).
- [50] T.M. Gür, H. Wise, R.A. Huggins, *Catal. Lett.* 23 (1994) 387.
- [51] J. Rutman, S. Raz, I. Riess, *Solid State Ionics* 177 (2006) 1771.
- [52] T. Hibino, A. Hashimoto, M. Yano, M. Suzuki, S.-I. Yoshida, M. Sano, *J. Electrochem. Soc.* 149 (2002) A133.
- [53] T. Hibino, A. Hashimoto, T. Inoue, J.-I. Tokuno, S.-I. Yoshida, M. Sano, *J. Electrochem. Soc.* 147 (2000) 2888.