

Reformer - Anode Assemblies in Medium Temperature Solid Oxide Fuel Cells

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Abstract: - Solid-oxide fuel cells (SOFC), especially those operating in the medium temperature range of 600 to 800°C are considered as promising devices for sustainable electrical energy production. SOFC may be supplied with a variety of fuels, among which are the liquid hydrocarbons; nevertheless these have to be reformed prior to their electrochemical oxidation (“combustion”) on the anode. This reforming process is endothermic, while the oxidation reactions taking place at the anode side are exothermic. Thus, the management of the cell interior heat exchange needs is a critical factor in cell operations and special reformer-anode configurations are required in order to develop compact, efficient and robust SOFC designs.

The typical «sandwich» type SOFC assembly is composed of three, functionally distinct layers (anode – electrolyte – cathode). These layers are characterized by their different porosity needs; the anode and cathode are required to have controlled porosity, while the electrolyte layer has to be non-porous. On the other hand, the reformer must be highly porous; such a structure is of particular interest because it facilitates an eventual reformer – anode integration.

This present work reviews the current technical literature on the choice of catalytic materials, as used for both the reforming of hydrocarbon fuels, considered as feedstock candidates for SOFC operations, and the electro-catalytic oxidation of reformats over the SOFC anode, from the viewpoint of their tolerance to sulphur presence in the fuel gas feed and carbon formation, during the reforming and oxidation reactions. The need for effective reformer-anode integration strongly suggests the physico-chemical compatibility of such materials or even direct oxidation of fuel over the anode surface. Such a possibility exists by the employment of composite oxide materials, such as those chosen from the perovskite-based structures, cubic fluoride-based structures, as well as the pyrochlores and spinels. The need, for the further optimization of their composition, is now very necessary.

Key-Words: - Solid oxide fuel cells (SOFC), reformer – anode assembly, sulphur tolerant anode materials

1 Introduction

The principle of the Solid Oxide Fuel Cell (SOFC) has been known since 1937 [1] but its practical realisation in an economically sustainable manner is still lagging and requires more dedicated research effort. The typical design embodiment is either tubular or planar «sandwich» configuration of an anode (fuel electrode), an electrolyte layer and a cathode (oxidant electrode). The low ($\approx 1V$) open circuit voltage of such cells

requires their stacking into multiple cell units which in turn implies use of additional layers of fuel and air distributors. But such «sandwich» structure of different types of nature materials, operating at temperatures of up to 1000°C, has its particular requirements concerning, among others: dimensional stability, chemical and thermal expansion coefficient compatibilities and adequate sealing arrangements between layers. In order to satisfy such stringent requirements, it is proposed to operate the cells at lower (500 – 800°C) temperatures.

The advantage of the SOFC concept over all other types of fuel cells, is its ability to operate with a variety of fuels both gaseous – such as methane, bio-gas, bio-syngas, and liquid – such as gasoline, jet fuel, diesel fuels and oxygenates, e.g. methanol, ethanol (and bio-ethanol) and “green diesel”.

Such a large range of feedstock makes the SOFC concept suitable for both stationary (as distributed generation [2] e.g. residential) and mobile (e.g. Auxiliary Power Units – APU) applications.

Hydrocarbons or oxygenated fuels both have to be reformed to create a $H_2 + CO$ mixture, prior to their “conversion” over the SOFC anode’s surfaces. Such a process is usually carried out in an external reformer, being a part of the overall plant (BOP) assembly. Analysis of the possibility of the internal steam reforming of methane has been carried out and it is concluded that there is sufficient heat available for the complete “conversion” of methane in the anode chamber [3]. However, techno-economic analysis of a 200kW SOFC cogeneration plant indicates, that a 50% reduction in the overall cost is possible if the external reforming is replaced by completely integrated, internal reforming [4].

The presence of sulphur and its derivatives in the fuel is a major concern because of their inhibitive effects on the catalytic activity of both the reformer and the SOFC anode and, as such, it requires a significant effort of desulphurisation prior to fuel conversion, either in the reformer or later, on the SOFC anode. Such a desulphurisation process is usually performed at the fuel treatment centre, prior to its further distribution, either by pipeline (for the natural gas case) or via a network of gas stations (for all liquid hydrocarbons and oxygenates). The residual sulphur content present in the “fossil fuel”, which may influence the choice of catalyst material, its structure and morphology for both the reformer and the SOFC anode, is usually controlled nationwide. However, its actual level in each type of fuel depends upon individual country’s legislation. From the collected data (Table 1), it is obvious that neither the current nor the future sulphur content, present in any of the “so far” analysed fossil fuels, will be less than 10ppm. Some alternative fuels, e.g. bio-syngas, landfill gas or sewage gas etc, are both “heavy” with sulphur derivatives (50-200ppm, 134mg/m^3 and 500ppm respectively) [5, 6] and halogen derivatives also. The presence of latter compounds requires such fuels to be “cleaned” prior their use in SOFC devices.

Table 1. The current and estimated future sulphur contents of the fuels, according to prevailing legislations.

Fossil Fuel	Sulphur Contents	
	Current	Future
<i>Natural gas*</i>	[mg/m^3]	[mg/m^3]
Canada & USA	15	15
European Union [7]	30	30
<i>Gasoline</i>	[ppm]	[ppm]
Canada [8] & USA	30 (annual average level) 80 (never-to-be-exceeded)	30 (annual average level) 80 (never-to-be-exceeded)
European Union	10	10
<i>Diesel fuel</i>	[ppm]	[ppm]
Canada [9] & USA	15 (since 1 July 2006)	<10 (mandatory from 2011)
European Union [10]	10	10
* Residual sulphur contents only – the sulphur derivative of odour additives are expected to be replaced by non-sulphur type [11] odorants;		

In an analysis of such reformer – anode assemblies, it is important to lay-out the corresponding to each module’s construction materials, structures and operational requirements. The anode, being the final process destination of the reformed fuel, will be discussed first.

2 SOFC Anode Processes

The role of the anode in a solid oxide fuel cell is to provide the “sites” for the input fuel gas to react with the oxygen ions, delivered to the “sites” by the electrolyte, within a geometric structure that also facilitates the necessary charge neutralisation through its high electronic conductivity [12].

2.1 Anode Materials Requirements

Materials considered as potential candidates for SOFC anodes need to display, apart from their capability for electrochemical oxidation of the fuel, associated with the charge transfer to a conducting contact, the following most desired characteristics [13]: electronic conductivity; oxygen diffusivity (ionic conductivity); oxygen surface exchange (reactivity); chemical stability and compatibility; compatible thermal expansion; mechanical strength and dimensional stability under redox cycling.

The catalytic properties of the anode material should not promote any unwanted side reactions (such as carbon formation on its surface) but should have to include its capability to sustain a high current density with low over-potential loss [14]. The latter point is related to the electrochemical reaction mechanism at the electrode, which involves both electron and ion transfer. While a solid electrolyte allows only ionic transfer the anode phase is necessary for the electron transfer, as well as a source/sink of material, so the fuel consumption is observed over the “so called” triple phase boundary (TPB) where, at the anode – electrolyte interface, the electrolyte delivered oxide ions are neutralized on the anode side. The longer the length of the TPB, the lower, the observed over-potential loss is [15].

2.2 Anode micro-structure

In order to satisfy the increased TPB length requirement, the microstructure of the anode needs to be organised to form an open but well connected framework, with anode material particles laid out on the electrolyte surface, thus allowing the fuel to circulate freely and easing the rapid evacuation of the electrochemical combustion products. The size of the anode particles has direct influence on the TPB length. Such a complex 3-D framework has a) to be easy to form at its production stage and b) has to be preserved during the entire life of the SOFC, this means no deterioration due to the thermal cycling and to possible exposure to air at high temperatures.

For the most investigated and the best performing anode – electrolyte systems (Ni - based cermets [16, 17]) the cell operation at about 1000°C causes modification of the fine morphology by undesired sintering of nickel particles. This phenomenon, that strongly affects the polarization behaviour of the electrode, may be limited by adding some wetting additives such as TiO₂, Cr₂O₃ or Mn₃O₄, to lower the interfacial energy between the YSZ and Ni [18]. The preservation of such nano-sized structure in the Nickel based anode may help to control

the carbon formation process observed over anode surfaces during the electrochemical combustion of hydrocarbons. While the carbon formation process due to Boudouard reaction $2\text{CO} \rightarrow \text{C} + \text{CO}_2$ may be limited by the cell’s operation temperature above 617°C [19], the carbon polymerization process, originating from the thermal pyrolysis of hydrocarbons, is favoured on large particles [20], known to initiate and promote this reaction. To increase the resistance of the nickel to carbon formation, originating from the fuel decomposition process, it is proposed [21] to limit the nickel particle size to less than 5nm, a size that coincides with the requirement of the TPB length control.

2.3 Sensitivity to sulphur present in a feed

Unfortunately, the majority of cermet based anodes are very sensitive to the residual sulphur present in the feed, and for Ni-doped zirconia based anodes, the rate of deactivation is directly proportional to H₂S concentration and is inversely proportional to the processing temperature. The mechanism of sulphur poisoning of the Ni-based anodes is illustrated in Fig.1 [22].

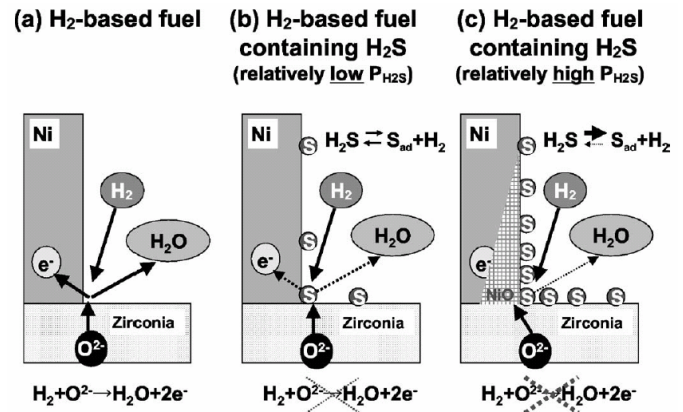


Fig.1 Sulphur poisoning mechanisms [22]: (a) H₂ – based fuel containing no H₂S (no poisoning), (b) H₂ based fuel with relatively low P_{H₂S}, in which the chemisorption of sulphur leads to a decrease in the electrochemical reaction sites and thus an increase in anodic polarization and cell voltage drop, and (c) H₂ – based fuel, with relatively high P_{H₂S}, in which further chemisorption of the sulphur leads to an oxidation of the Ni anodes and thus an increasingly large anodic polarization and corresponding cell voltage drop (for a given current density).

In an attempt to control the sulphur tolerance, some additives (Ce, Ti, Sc, Y, Nb, Mg, Ca, La, or Al, as

oxides, and Ru or Co as “free metals”) were impregnated into Ni-cermet anodes but only with limited success [23]. Some additions of Mo and W were tested as well [24].

The polarization impedance and the DC over-voltage of the Ni-YSZ cermet anode, are increased when the H₂S concentration exceeds 0.05, 0.5 and 2ppm at 1023, 1173 and 1273 K, respectively [25]. The deactivation is very rapid – the saturation of the sulphide influence is almost independent of sulphide impurity concentration, and is found to be about 12, 9 and 4ks at 1023, 1173 and 1273 K, respectively.

The sulphur tolerance test, carried out for 90min with simulated bio-syngas containing up to 9ppm of H₂S over the Ni-GDC anode, indicated no impact on the anodic impedance [26]. This was probably because doped ceria is not affected by H₂S, but nickel, having higher affinity for sulphur, was playing the role of an electronic conductor. Similar short term (1hr and 24hrs) experiments, with Ni-YSZ anode, and fed with up to 240ppm of H₂S laden bio-syngas, resulted in linear voltage drop with increasing sulphur concentrations from 0 to 60ppm H₂S, and no further drop for H₂S concentrations above 80-100ppm [27].

Integrated planar Ni-based SOFC modules, when operated with H₂S contaminated and humidified H₂, have experienced important deactivations. The extrapolation of the permissible sulphur concentration in the natural gas feed, considering a deactivation rate of 0.75% per 1000h (6.4% per year) has indicated the value of 18ppb [28]. Such a “deep” desulphurization treatment of fuel will be totally impractical from the technological point of view.

There are many research efforts being made to increase the sulphur resistance of nickel based cermet anodes, e.g. alloying [29] of Ni with Cu and Fe or, to replace it completely by another metal such as Cu [30]. However the still significant presence of metallic phases in the anode will provoke considerable expansion and contraction upon redox cycling, leading to internal stresses and possible exfoliation/delamination of the anode. Such exposure of the anode to air is very useful in order to remove carbon and sulphur deposits formed over the anode surface after prolonged operation of the SOFC units.

In the search for replacement of the limited use Ni-YSZ, or other cermet anodes, the mixed ionic-electronic conductivity (MIEC) ceramics have been identified as possible candidates. The advantage of these ceramics is that the fuel consumption is no longer limited to the TPB zone but is spread over the entire surface of the

anode [31], easing up on the stringent requirements concerning the anode-electrolyte TPB interface formation. Such mixed conductivity can be introduced, either by “doping” or by stoichiometry changes introduced into the anode material.

Many MIEC ceramics have already been so identified [32, 33] among the few groups of materials, such as:

- perovskite-related structures (titanates, chromites, vanadates, gallates, niobates and ferrites),
- cubic fluorite structures (zirconia-based and ceria-based) and
- other oxide structures (pyrochlores, spinels).

It is to be expected that some types of such ceramics will exhibit a more sulphur tolerant behaviour, a point that has already received some confirmation:

- the perovskites-based Sr_{0.6}La_{0.4}TiO₃/YSZ (50/50wt%) anode, operating at 1000°C, exhibited no degradation of performance in the presence of up to 5000ppm of H₂S in the hydrogen fuel [34], and an even further exposure for 8 hours to 1% H₂S concentration in hydrogen, did not deteriorate its performance;
- the perovskite-based La_xSr_{1-x}VO_{3-δ} anode exhibited [35] interesting sulphur tolerance values, once exposed to 5% H₂S – 95% H₂ fuel at 1000°C, with no significant deterioration during 48h test period becoming evident;
- for the perovskite-based Sr₂MgMoO_{6-δ} anode [36], exposed to both 5 and 50ppm H₂S in H₂, the loss in output was only about 0,1% after 2 days and 4,8% after 200 hours respectively;
- the pyrochlore-based Gd₂Ti_{1.4}Mo_{0.6}O₇ anode showed [37] remarkable tolerance to up to 10% H₂S in H₂, when operating at 950°C for six days. Such “stunning” results suggest that good catalytic activity of this material towards the oxidation of H₂S needs closer examination.

Nevertheless, the resistance of such MIEC anodes to very high sulphur contents is not guaranteed; i.e. the resistance to sulphur poisoning of the La_{0.75}Sr_{0.25}Cr_{1-x}Mn_xO₃ anode increased [38] with the content of Cr but such anodes failed after exposure to 10% H₂S in H₂ for 5 days.

3 Fuel Reforming vs Direct Oxidation over Anode Processes

The reforming process, while known for almost a century as the synthesis gas production route, is still a subject of intensive studies [39]. The existing catalytic

reforming process has two important shortcomings: 1) the formation of carbon deposits over the transition metal catalyst and 2) catalyst's sensitivity to the presence of sulphur in the hydrocarbon feed. The mechanisms of such "carbon like" deposits formation are identified [40] as:

1. Formation of amorphous flakes and filamentous carbon, due to carbon monoxide decomposition (according to the Boudouard reaction).
2. Formation of encapsulating carbon, due to the direct decomposition of hydrocarbons.
3. Pyrolytic carbon, originating from the thermal cracking of hydrocarbons.
4. Soot formation in the sub-stoichiometric methane oxidation process.

As previously explained, the size of the nickel particles is very important from the viewpoint of the carbon formation. To increase the resistance of nickel to carbon formation, originating from the fuel decomposition process, it is proposed [21] to limit the nickel particle size to less than 5nm. The alloying of the nickel with some small (<1% w/w) amounts of Sn [41], or indeed the noble metals, such as Au [42] or Pt, Pd and Ir [43], presumably makes such catalysts more robust by blocking highly reactive Ni "edge and kink" sites by ad-atoms. Nickel supporting oxide, (such as Ceria [44]) skeleton may play a very important role in the re-oxidation of the "depositing carbon". The Samarium Doped Ceria (SDC) modified nickel anode surface was performing very well in its carbon deposition prevention role [45].

While the routes to carbon formation control are numerous, including the use of H₂O in excess, the resistance to the presence of sulphur in the fuel is more difficult to achieve. Recently, it has been shown that impregnation of nickel with a sulphur bearing compound, e.g. *n*-alkanethiols [46], can be used as a means for controlling the reactivity of Ni.

Apart from the sulphur intolerance of metallic (especially Ni-based) catalysts, their imposition of high reforming reaction rate, makes the local heat balance, with anode oxidation reaction, difficult [47]. The "mismatch" in the rates of the reforming reaction and the anode oxidation can lead to undesirable local cooling, and hence, to thermal stresses causing delamination /exfoliation of the anode.

3.1 The integrated (indirect) internal reforming

The integrated (or indirect) internal reforming SOFC requires special care to ensure that appropriate thermal contact between reformer and SOFC is obtained. One

solution towards this goal is to intercalate the reformer with SOFC (Fig.2)

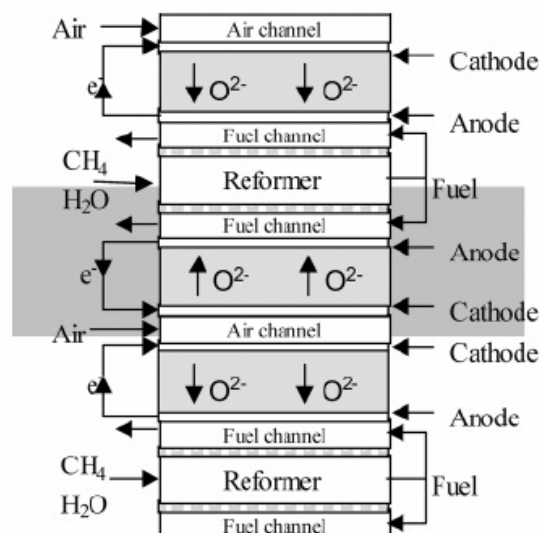


Fig.2. Proposed [48] reformer-SOFC configuration.

Such a configuration, while easing the heat balance problems, makes the gas circulation relatively complex. The best solution proposed up to the present is to gradually internally reform the fuel (Fig.3) by local association of a catalyst used for steam reforming and another for the H₂ electrochemical oxidation. Such a microstructure permits reducing the diffusion resistance and thereby, achieving the same production rate within a smaller reactor bed [49]. In the conventional honeycomb catalysts structures, the reforming process is mass-transport limited.

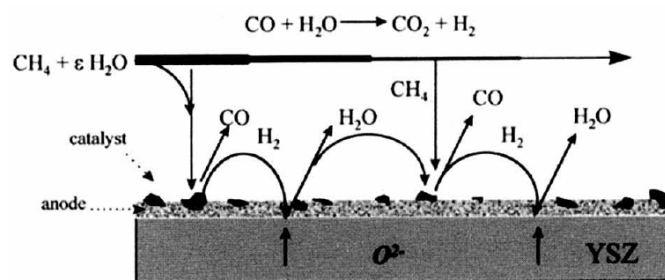


Fig.3. Diagram of the gradual internal reforming process [50].

The use of oxide catalysts (e.g. high surface area ceria) to produce hydrogen, from the autothermal steam reforming of LPG (propane/butane), is reported [51]. The main products (at 900°C) from steam reforming

were: H₂, CO, CO₂, and CH₄, along with a small amount of C₂H₄. The addition of oxygen in the autothermal reforming appreciably reduced the degree of carbon deposition and eliminated the C₂H₄ formation.

3.2 The direct oxidation over the anode surface

Direct oxidation over the SOFC anode is technically the most interesting solution and has frequently been reviewed [52, 53]. Some early efforts were based on simple oxides, such as ceria [54] or SDC [55] but this research work was soon extended to more complex and elemental substitution permitting, like perovskite-type, structures [56]. These are known for their catalytic performances [57] and are widely exploited in the chemical industry. The most recent papers address both structural/electrochemical investigations of new oxide formulations such as Sr₂FeNbO₆ [58], LaSrCoFeO [59], (La_{0.75}Sr_{0.25})_{0.95}Cr_{0.5}Mn_{0.5}O_{3-δ} [60] and the direct fuel oxidation applied to methane [61-63] or diesel fuel [64]. The all-perovskite (anode, electrolyte and cathode) SOFC may be of particular interest. Such fuel cells [65], based on the “sandwich” of the (La_{0.75}Sr_{0.25})_{0.95}Cr_{0.5}Mn_{0.5}O_{3-δ} (LSCM) as the anode, La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.15}Co_{0.05}O_{3-δ} (LSGMCo) as the electrolyte and Gd_{0.4}Sr_{0.6}CoO_{3-δ} (GSC) as the cathode, can minimize the polarization losses between electrolyte and electrodes, where the slight inter-diffusion between the perovskite components observed results in better contact at the interface, allowing for smoother transfer of oxygen ions between the electrodes and electrolyte.

4 Conclusions

The extreme sensitivity of cermet based anodes to the presence of residual sulphur in the fuel, and the technical incapacity of the hydrocarbon industry to produce the desired sulphur freeⁱ fuels at market acceptable prices (except biomass like fermentation derived oxygenates) makes the sulphur tolerant, composite oxide based anodes an interesting alternative approach. Among the candidates are:

- perovskite-related structures (titanates, chromites, vanadates, gallates, niobates and ferrites),
- cubic fluorite structures (zirconia-based and ceria-based) and
- other oxide structures (pyrochlores, spinels).

ⁱ «sulphur free» means 0 ppmw sulphur, contrary to [9], where it means less than 10 ppmw of sulphur.

Such a variety of structures, especially in the case of the ABO₃ perovskite-type oxides with a possibility of A_{1-x}A'_xB_{1-y}B'_yO₃ substitutions, renders the systematic structural and electrochemical studies very lengthy. The use of the combinatorial chemistry method [66], for elemental composition optimization (method already successfully applied to the optimization of the catalytic conversion of ethanol [67]), will certainly accelerate the research efforts.

The extension of the recently published work [68] on the fundamental research of the interaction of sulphur bearing compounds with catalytically active metals and oxides, to more complex and less-defined oxide surfaces, will be helpful in guiding the research community over the choice of materials and will avoid some hurdles of the composite oxide synthesis processes.

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