

Advances in catalysts for internal reforming in high temperature fuel cells

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Abstract

Catalytic steam reforming of natural gas is an attractive method of producing the hydrogen required by the present generation of fuel cells. The molten carbonate (MCFC) and solid oxide (SOFC) fuel cells operate at high enough temperatures for the endothermic steam reforming reaction to be carried out within the stack. For the MCFC, the conventional anodes have insufficient activity to catalyse the steam reforming of natural gas. For these cells, internal reforming can be achieved only with the addition of a separate catalyst, preferably located in close proximity to the anode. However, in the so-called 'Direct Internal Reforming' configuration, attack from alkali in the MCFC may severely limit catalyst lifetime. In the case of the state-of-the-art SOFC, natural gas can be reformed directly on the nickel cermet anode. However, in the SOFC, temperature variations in the cell caused by the reforming reaction may limit the amount of internal reforming that can be allowed in practice. In addition, some external pre-reforming may be desirable to remove high molecular weight hydrocarbons from the fuel gas, which would otherwise crack to produce elemental carbon. Degradation of the SOFC anode may also be a problem when internal reforming is carried out. This has prompted several research groups to investigate the use of alternative anode materials. © 1998 BG plc. Published by Elsevier Science S.A.

Keywords: Fuel cells; Hydrogen; Natural gas; Internal reforming; Catalysts

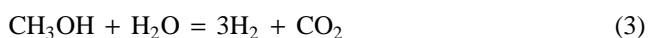
1. Introduction

Steam reforming is a well-established industrial process for producing hydrogen or synthesis gas from natural gas, other hydrocarbon fuels and alcohols. Numerous reviews have been published [1–3]. For methane, the reforming reaction Eq. (1), and associated shift reaction Eq. (2) are carried out at elevated temperatures over a supported metal catalyst, usually nickel:



Steam reforming of methane is highly endothermic, and the large scale industrial process is carried out typically above 700°C, to ensure an adequate rate of reaction, and to maximise hydrogen production which, from reaction Eq. (1), is thermodynamically favoured by high temperatures and low pressures. Reactions similar to Eq. (1) may be written for other hydrocarbons. Over an active catalyst, the products of steam reforming are dictated by the thermodynamic equilibria set up between reactions Eq. (1) and Eq. (2).

Alcohols may also be steam reformed, for example methanol:



With alcohols, which are, in general, more reactive than hydrocarbons, the reaction may be carried out at lower temperatures. Methanol can be steam reformed at around 250°C over a Cu/ZnO catalyst.

Fuel cell developers have for many years known that the heat required to sustain the endothermic reforming of low molecular weight hydrocarbons (e.g. natural gas) can be provided by the electrochemical reaction in the stack. This has led to various elegant internal reforming concepts which have been applied to the molten carbonate (MCFC) or solid oxide (SOFC) fuel cells, on account of their high operating temperatures. The various approaches that developers have adopted for internal reforming are reviewed in Section 2 below.

For the MCFC, internal steam reforming catalyst may be required to operate under conditions where degradation caused by poisoning due to alkali from the electrolyte may limit the stack lifetime. Section 3, therefore, provides a review of recent advances in catalyst formulation for the MCFC together with development of porous shields which are intended to protect the catalyst from attack by alkali. A nickel/YSZ cermet anode is used in the state-of-the-art high temperature SOFC. This, in itself, may provide an adequate catalyst for the steam reforming and shift reactions. The issues surrounding internal reforming in the SOFC are reviewed in Section 4. In all cases of steam reforming,

there is a risk of carbon formation, and this is discussed in Section 5.

2. Approaches to internal reforming

Developers of internal reforming fuel cells have generally adopted one of two approaches; these are usually referred to as direct (DIR) and indirect (IIR) internal reforming. They are illustrated schematically in Fig. 1. In some cases a combination of both approaches have been taken. A thermodynamic analysis and comparison of the two approaches to internal reforming in the MCFC has recently been completed by Freni and Maggio [4].

2.1. Indirect internal reforming (IIR)

Also known as integrated reforming, this approach involves conversion of methane by reformers positioned in close thermal contact with the stack. An example of this type of arrangement [5] alternates plate reformers with small cell packages. The reformate from each plate is fed to neighbouring cells. IIR benefits from close thermal contact between stack and reformer but suffers from the fact that heat is transferred well only from cells adjacent to the reformers and steam for the reforming must be raised separately. A variation of this type of arrangement places the reforming catalyst in the gas distribution path of each cell [6]. With IIR the reforming reaction and electrochemical reactions are separated.

2.2. Direct internal reforming (DIR)

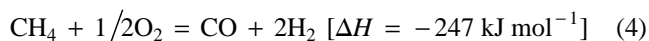
In direct internal reforming, the reforming reactions are carried out within the anode compartment of the stack. This can be done by placing reforming catalyst within the fuel cell channels in the case of the MCFC, but for the SOFC the high temperature of operation and anode nickel content of most SOFCs mean that the reactions can be performed directly on the anode. The advantage DIR is that not only does it offer good heat transfer, but there is also chemical integration – product steam from the anode electrochemical reaction can be used for the reforming without the need for

recycling spent fuel. In principle, the endothermic reaction can be used to help control the temperature of the stack, but this effect is not enough to completely offset the heat produced by the electrochemical reaction and management of the temperature gradients is an issue. Examples of the use of direct internal reforming are to be found in the Westinghouse 25 kW SOFC prototype [7] and in various DIR–MCFC concepts [8].

In contrast to the steam reforming reaction Eq. (1), the fuel cell reactions are exothermic, mainly due to heat production in the cell caused by internal resistances. Under practical conditions, with a cell voltage of 0.78 V, this heat evolved amounts to 470 kJ/mol CH₄ [9]. The overall heat production is about twice the heat consumed by the steam reforming reaction in a IR cell. Hence, the cooling required by the cell, which is usually achieved by flowing excess gas through the cathode in the case of external reforming systems, will be much smaller for internal reforming systems. This has a major benefit on the electrical efficiency of the overall system. Application of internal reforming offers several further advantages compared with external reforming. These have been reviewed elsewhere [10].

2.3. Catalytic partial oxidation (CPO)

Catalytic partial oxidation is another approach that may be viewed as variant of steam reforming. In CPO, a small amount of oxygen, usually air, is admitted with fuel to a catalytic reactor in which exothermic reactions of the following type occur:



Partial oxidation is usually less efficient than steam reforming for fuel cell applications, for two reasons. Firstly reaction Eq. (4) is effectively the summation of the steam reforming and oxidation reactions; about half of the fuel that is converted into hydrogen is oxidised to provide heat for the reaction. Secondly, if air is used as the oxidant, this results in a lowering of the partial pressure of hydrogen at the fuel cell. A key advantage of CPO, however, is that it does not require steam. It may, therefore, be considered for applications where system simplicity is regarded as more important than high electrical conversion efficiency, for example small scale cogeneration.

3. Internal reforming in the MCFC

Internal reforming can be carried out in an MCFC stack provided a supported metal catalyst is incorporated. This is because the conventional low surface area porous nickel anode has insufficient catalytic activity to support the steam reforming reaction at the 650°C operating temperature. Several groups demonstrated internal reforming in the MCFC in the 1960s [11] and identified the major pro-

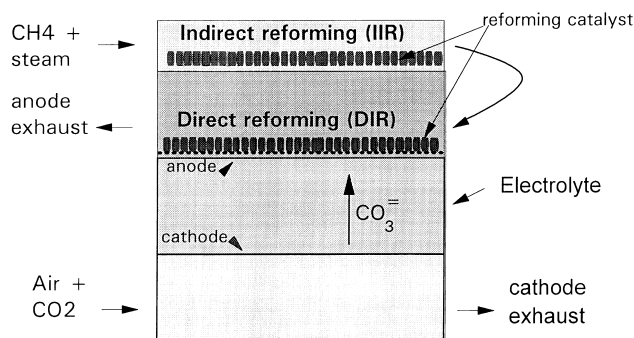


Fig. 1. Approaches to internal reforming (DIR and IIR) in the MCFC.

blem areas to be associated with catalyst degradation, caused by carbon deposition, sintering and catalyst poisoning. Development was pursued in the 1970s and 80s in the US, notably at IGT in Chicago, and there has been recent awakening of interest in internal reforming in Europe and Japan.

In Europe, BCN (Dutch Fuel Cell Corporation) is now leading an 'Advanced DIR–MCFC development' under a European Union supported programme [12], in which British Gas (BG) is carrying out the catalyst development. Another major group of companies (ARGE) is developing internal reforming systems, with one of the project partners, Haldor Topsoe (Denmark), developing the internal reforming catalyst. The third major European partnership, led by Ansaldo, does not employ internal reforming, but uses an external sensible-heat reformer [13].

Mitsubishi Electric Corporation is the principal developers of direct internal reforming MCFC stack technology in Japan. However, several other companies such as Sanyo, have developed non-reforming and IIR MCFC stacks. Sanyo and Tonen have also recently developed an interest in IR catalyst technology.

In the US, MCFC technology is being developed principally by two main companies, Energy Research Corporation and MC-Power Corporation. Both are well advanced in promoting demonstrations of MCFC technology at the 250 kW–2 MW scale. ERC utilise internal reforming stacks (a combination of IIR and DIR) whereas MC-Power are currently focused on using external reforming stacks in conjunction with plate reformers.

3.1. Key requirements for MCFC reforming catalysts

3.1.1. Sustained activity to achieve the desired cell performance and lifetime

For use in an MCFC, steam reforming catalyst needs to provide sufficient activity for the lifetime of the stack so that the rate of the reforming reaction is matched to the rate of the electrochemical reaction, which may decline over a period of time. The strongly endothermic reforming reaction causes a pronounced dip in the temperature profile of an internal reforming cell which is most pronounced for the DIR approach. Optimisation of reforming catalyst activity is important to ensure that such temperature variations are kept to a minimum, to reduce thermal stress, and thereby contribute towards a long stack life. Improvements in temperature distribution across the stack may also be achieved through the recycle of either anode gas, or cathode gas, or indeed both.

3.1.2. Resistance to poisons in the fuel

Natural gas, which is principally methane, is the fuel of choice for the MCFC, but other fuels such as other hydrocarbons (LPG, propane, naphtha) or alcohols (methanol) may be used. However, most raw hydrocarbon fuels (including natural gas) contain impurities (e.g. sulphur compounds)

which are harmful for both the MCFC anode and the reforming catalyst. The tolerance of most reforming catalysts to sulphur is very low, typically in the ppb range.

3.1.3. Resistance to alkali/carbonate poisoning

In the case of DIR catalysts which are located close to the MCFC anode there is a risk of catalyst degradation through reaction with carbonate or alkali from the electrolyte. This is described in more detail below, and it has provided the biggest challenge to internal reforming catalyst developers. In contrast, many commercial steam reforming catalysts are available that will fulfill the duty of an IIR-MCFC system, and it is therefore not surprising that most MCFC developers have adopted the less demanding IIR approach.

3.2. Reaction kinetics and mechanisms of internal reforming in the MCFC

Designers of internal reforming systems need to know the rate of the reforming reaction at the stack operating conditions, since this allows the system to be optimised. It enables the degree of anode recycle, and balance of internal vs. external reforming to be set.

Kinetic studies [14] and deuterium exchange experiments [15,16] have indicated that the reaction mechanism of steam reforming on nickel involves the dissociative chemisorption of methane to form surface carbon species. For most hydrocarbons this assumes a two site mechanism except for methane where no adsorbed molecule is necessary as the precursor. In the case of methane conversion over nickel, an adsorbed CH_3^* species is converted to an adsorbed carbon atom through stepwise dehydrogenation [17]. The adsorption of methane has been generally thought of as the rate determining step [10] and this is consistent with the many kinetic studies which have indicated first order kinetics in methane.

However, use of a simple first order rate equation for internal reforming in the DIR–MCFC does not take into account the influence of the electrochemical reaction which consumes the products of reaction (H_2 and CO) and liberates oxygen in the form of carbonate ions at the anode. Another aspect to consider with steam reforming in the MCFC is the effect of mass transfer. Kinetic studies by Berger [18] and BG suggest that at MCFC temperatures, the reforming reaction is largely diffusion controlled when conventional pelleted catalyst is used.

3.3. Effects of alkali on DIR catalysts

It has been known for many years that carbonate in the MCFC electrolyte may poison steam reforming catalyst if it is located within the anode chamber [19,20]. Poisoning of catalyst by alkali arises through transport either by liquid creep along solid components (e.g. the walls) of the MCFC stack, or via a vapour phase diffusion mechanism. In the latter case there is substantial evidence that carbonate pre-

sent in the pores of the electrolyte evaporates as an alkaline hydroxide. The two mechanisms are illustrated in Fig. 2. Recent experimental evidence by Berger et al. [21] suggests that vapour phase transport is the predominant mechanism under DIR–MCFC conditions.

Development of direct internal reforming catalysts has mainly concentrated in the past on nickel supported on alkali-resistant materials such as MgO [22–24] and LiAlO_2 , many of which have been shown to be successful for internal reforming of methane. However, Berger et al. [21] point out that for many of the early studies operating times were rather short and/or the test conditions were less severe than normally encountered under practical conditions.

Interestingly, potassium is well-known as a promoter in steam reforming catalysts; it is often added to reduce the risk of carbon deposition by decreasing the acidity of the catalyst support, which would otherwise promote the hydrocarbon cracking reactions. Recent quantum mechanical calculations [25] have shown that adsorbed potassium atoms on the nickel(III) surface have a pronounced effect on the electronic properties of the surface nickel atoms, although the implications for the steam reforming reaction are not yet well understood. Kitabayashi has shown that smaller amounts of potassium (1–2 wt%) added to a Ni/MgO catalyst as K_2CO_3 may result in an increase in the surface nickel concentration although the steam reforming activity falls. Rostrup Nielsen [25] has shown that alkali does not apparently affect the sintering of nickel crystallites under reforming conditions. He attributes the observed enhancement of sintering of nickel in some catalysts by alkali to the effect of alkali on the support.

MgO catalysts have been investigated in some detail by Cavallaro et al. [23] who have shown that in a DIR–MCFC test lasting 860 h, alkali deactivates the catalyst by a pore blocking mechanism. A glassy layer of KOH was formed which covered the whole of the external surface of the pellets, preventing access to the active sites.

3.4. Development of protective shields

In the DIR–MCFC it may be possible to extend the life-

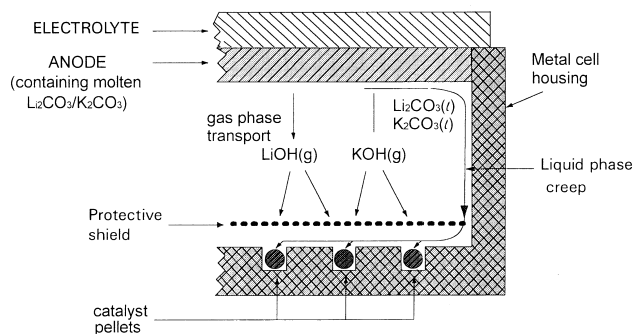


Fig. 2. Mechanisms for alkali transport in the internal reforming MCFC.

time of existing catalysts by protecting the catalyst from alkali attack by inserting a protective shield between the anode and the catalyst. One of the earliest proposed devices was a thin plate of nickel that is porous to hydrogen and steam but impervious to alkali [26–28]. More recent applications of the nickel foil concept have been proposed by workers at Sanyo [29,30]. Hitachi have proposed the use of a sintered nickel fibre or a porous ceramic [31]. Tonen have tested metals and alloys of Ni, Co, Au, Cu, Ag or the platinum group in the form of a micro-porous plate with a thickness of 0.03–1 mm [32]. Toshiba claim that B_4C , HfN, ZrO_2 can repel alkali but can be made porous to H_2 and H_2O [33]. Most recently, Passalacqua et al. [34] have reported the preparation of a series of ceramic membranes for shielding the catalyst. A sample of SiC membrane 0.32 mm thick performed as an effective alkali shield for a test duration of 700 h and post-test analysis showed there had been no significant change in microstructure during use. Energy dispersive X-ray analysis of the used material also showed that some potassium was retained by the membrane. Such work demonstrates that, in principle, it is possible to engineer a catalyst shield for the DIR–MCFC but further work will be needed to optimise the design and to prove its durability in the long term.

3.5. Development of alternative catalysts

Although work continues on nickel-based DIR–MCFC catalysts [35], precious metal catalysts have recently been investigated, particularly for the direct internal reforming of light hydrocarbons such as LNG, LPG naphtha and kerosene, where the risk of carbon deposition via hydrocarbon cracking is greater. Tonen have proposed and tested various supported metals of which ruthenium and rhodium were found to be especially stable [36–38]. In conjunction with Sanyo, Tonen have shown that deactivation of Ru/ ZrO_2 catalyst over a period of 2700 h is very small [39].

3.6. DIR–MCFC catalyst research at BG

3.6.1. Out-of-cell catalyst tests

Work has been carried out by BG Research and Technology to identify catalysts that are capable of extended operation for the direct internal reforming of natural gas [40]. Several catalyst types have been examined, usually nickel or ruthenium, supported on $\gamma\text{-Al}_2\text{O}_3$, SiO_2 , or MgO, with various promoters.

To assess the resistance of these catalysts to deactivation by alkali, a small-scale ‘out-of-cell’ tubular reactor test was devised, to mimic conditions encountered within the DIR–MCFC [40,41]. Two series of tests were carried out. In the first, catalyst was loaded as 3 mm pellets in a vertical reactor tube (Fig. 3) supported and surmounted by α -alumina pellets. For the second series of tests the catalyst was loaded in an intimate mixture with 3 mm α -alumina pellets doped with a mixture of alkali carbonates corre-

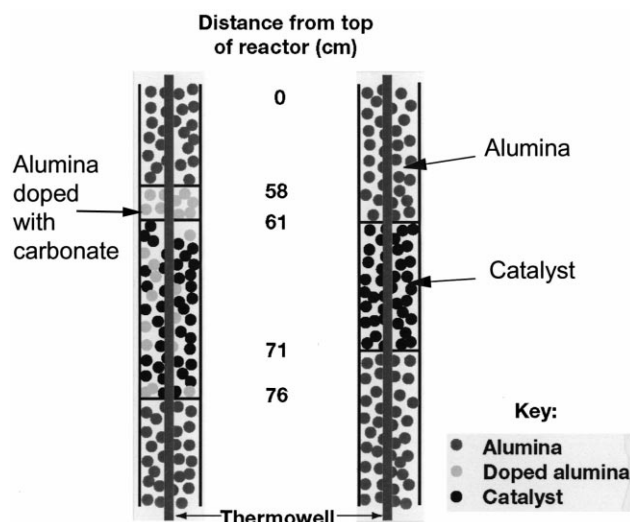


Fig. 3. BG Out-of-cell test reactor.

sponding to the mixture used in the cell electrolyte. The aim was to simulate the environment in a molten carbonate fuel cell, and to accelerate degradation of catalyst by alkali, by having the catalyst in close contact with the carbonate mixture.

Several tests in both carbonate and non-carbonate environments demonstrated that the method provided a means of assessing reforming activity. Differences in activity could easily be judged from the shape of the temperature profiles recorded at intervals throughout each test. Examples of temperature profiles recorded from a Ni/ γ -alumina catalyst performing well in a lithium/sodium carbonate environment are shown in Fig. 4. The endothermic nature of the steam reforming reaction is shown as a temperature dip in the first few centimetres of the catalyst bed. If the catalyst is experiencing little or no deactivation, the position of the endotherm would not be expected to move very much during the course of the test, and this was the case in the example shown in Fig. 4.

Most out-of-cell tests were carried out for 1000 h. During this timescale it was possible to judge catalyst deactivation by the movement and elongation of the temperature dip. Analysis of product gases also confirmed the activity of the catalyst during such tests. The out-of-cell tests were used to initially screen a series of candidate internal reforming catalysts. Those which performed well under a carbonate environment were then subject to more detailed tests in laboratory scale (10×10 cm) fuel cells.

3.6.2. Laboratory scale MCFC tests

Laboratory scale tests were carried out by ECN [40] with characterisation of the catalysts being undertaken by BG. The bench-cells consist of a pair of machined, stainless steel flanges with headers and piping for the gas supply. Each flange was machined with channels for distributing the gases. A set of porous cell components, together with a

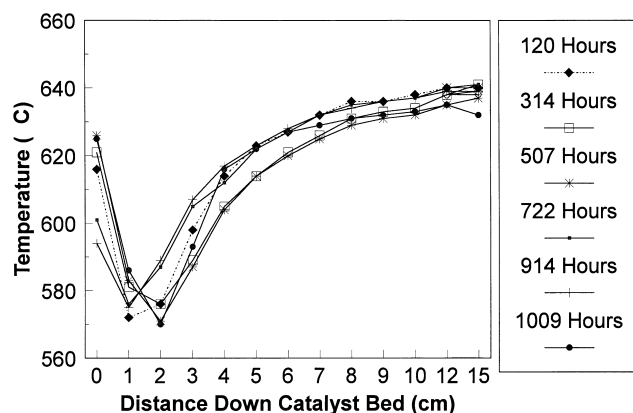


Fig. 4. Temperature profiles measured in BG out-of-cell test.

pair of current collectors was sandwiched between the flanges. Steam reforming catalyst was located in the gas distribution channels of the anode flange.

As a rule, each bench-cell experiment was operated under non-reforming conditions for several days after reaching the operating temperature. Similarly at the end of an experiment before cooling down, the cell is operated under non-reforming conditions. This procedure was followed to make a distinction between performance decay due to catalyst deactivation vs. degradation of the porous components.

Routine measurements carried out during the tests, included $V-I$ curves, internal resistance (by the current interruption method) and product gas analyses. The latter enabled the methane conversion to be determined under open circuit (OCV) conditions. Except when such measurements were being taken, the cell was operated continuously under load at 150 mA cm^{-2} .

Tests of 1000 h duration at temperatures of 600, 650 and 700°C were carried out. These demonstrated that at lower temperatures the catalyst exhibits slower deactivation than at higher temperatures. This is in agreement with work recently carried out by Mitsubishi [42] and confirms the earlier findings by Baker et al. [43].

Fig. 5 shows the deactivation of three types of catalyst that were tested for 1000-h bench scale DIR-MCFC tests. Catalyst F was a commercial nickel/calcium aluminate high temperature steam reforming catalyst, H was a nickel/ γ -alumina catalyst prepared by a deposition precipitation method [18] and catalyst B was a co-precipitated nickel/ γ -alumina stabilised by a proprietary BG method.

An additional series of tests using catalyst B, carried out for periods up to 5000+ h has shown that the nickel crystallite size increased from an initial value of below 50 up to 800 \AA . In addition, the alkali uptake increased to a level of several percent, although the catalyst still retained a large steam reforming activity.

3.6.3. Analysis of discharged catalyst

Upon completion of each out-of-cell test, the catalyst was cooled to ambient temperature in flowing hydrogen and then

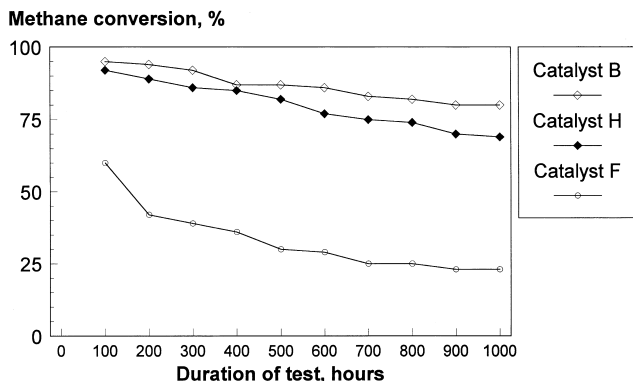


Fig. 5. Results of three 1000-h DIR cell tests.

passivated by admitting carbon dioxide. Various chemical and physical analyses [10,40] were then carried out to study the effect of deactivation by alkali.

X-Ray diffraction measurements show that, in general, the discharged catalysts from the carbonate tests had higher nickel crystallite sizes, and lower total and metal areas than those tested in the absence of carbonate. However, these differences were not great, except perhaps for a Ni/MgO catalyst where the nickel crystallite sizes were substantially greater. Area and crystallite sizes did not change much over the 1000-h period indicating that the catalysts are relatively stable over much of the test period and that any loss in activation occurs over a few hours at the start of a test. A similar behaviour was also found in the non-carbonate tests.

Transmission electron microscopy (TEM) on catalyst discharged from the first series of 'out-of-cell' tests (conducted in the absence of molten carbonate), indicated that there is little difference in particle size between catalysts H and F after 1000 h. However catalyst B exhibited both a smaller particle size range and a smaller mean particle size than the other catalysts. This leads to the conclusion that the level of sintering exhibited by catalyst B is less than that of either F or H.

Some conclusions may also be drawn regarding the influence of operating temperature and duration of test. As other workers have found [42], increasing the operating temperature from 600, to 650 and 700°C, does influence the average nickel particle size. Discharged samples from 1000-h runs show that the average crystallite size increases with temperature. Similarly regarding duration of test, analysis of catalysts from bench-scale tests run for different times (100, 1000 and 5000 h) show that the mean particle size increases with time, at least up to 1000 h.

Samples of catalysts that had been tested in 'out-of-cell' tests in the presence of carbonate were also examined by TEM/EDX and by surface science techniques to ascertain the fate of the alkali that is taken up by the catalyst during use. It was found that in all cases (catalysts B, F and H) the potassium becomes associated with the γ -alumina support, even after only 50 or 100 h of operation. It is worth noting that even with alkali uptakes as high as ca. 9% by weight in

a cell test lasting over 5000 h, catalyst B retained a high steam reforming activity.

In contrast to the nickel/ γ -alumina catalyst, a nickel/magnesia catalyst in out-of-cell tests experienced severe deactivation which can be linked to the collapse of the support [41]. After 200 h the total surface area, measured by nitrogen adsorption, dropped from 30 to 1 m² g⁻¹, and a substantial decrease in the nickel surface area also occurred.

Results from ECN and BG have shown that out-of-cell tests produce a more severe environment than in-cell tests, and that they provide a realistic and stringent 'screening' process for DIR-MCFC catalysts. The levels of potassium deposited on catalysts from out-of-cell tests were in some cases three times greater than those from in-cell tests of the same duration.

Bench scale tests longer than 5000 h have now been conducted which have led to the demonstration of the DIR-MCFC catalyst in stacks of 1 and 2 kW [40,44].

4. Internal reforming in the SOFC

4.1. Key requirements

4.1.1. Stable anode material for reforming and good electronic conductivity

The material chosen for the SOFC anode must be chemically stable not only be at the fuel inlet conditions, but also be stable at the more oxidising fuel outlet conditions. The low oxygen partial pressure in the anode compartment allows the use of metals for the anode material. Metals that could be used include nickel, cobalt and the noble metals, although most workers have followed the example of Westinghouse and used Ni-YSZ (YSZ = yttria stabilised zirconia). This is due to the relatively low cost

of nickel together with its high activity for the electrolytic oxidation of hydrogen [45]. One of the problems with Ni-YSZ is that for compositions of high electrical conductivity (above 30% Ni), the thermal expansion coefficient does not closely match that of the YSZ electrolyte, which may lead to the introduction of intolerable thermal stresses. There is a need, therefore, to improve the conductivity of anode materials, especially if the operating temperature of the cell is reduced. Steele [46] has also pointed out that the method of fabrication may influence the long term stability of Ni-YSZ cermets. The chemical vapour deposition (CVD) methods adopted by Westinghouse have led to materials that are stable for at least 30 000 h, whereas anodes prepared by depositing NiO-ZrO₂ followed by a reduction step have yet to be demonstrated for long periods.

4.1.2. Tolerance to large temperature gradients

As nickel is a good steam reforming catalyst, internal

reforming can be carried out directly on a Ni-YSZ anode. However, this can cause problems because at the current high temperatures of the SOFC (above 800°C) the reforming rate is so fast that a large temperature drop can occur at the inlet of the cell. This effect can be minimised by applying anode recycle, as with the MCFC. Another technique is to admit the fuel in stages along the cell. This is more easy to achieve with tubular geometries and has been applied by Westinghouse. A further method is to design the anode material with a lower steam reforming activity, but in this case there may be a conflict with the need to maintain good electrical conductivity.

4.1.3. Robust reduction, start up and shut down behaviour

Reduction and conditioning of the anode cermet must be considered. It is well known that the reduction regime of nickel steam reforming catalysts influences the performance of the final catalyst [2].

4.2. Steam reforming kinetics on SOFC anodes

As with the MCFC reforming catalyst, knowledge of internal reforming kinetics is important for the stack developer. Some of the factors that influence reforming rate are discussed below:

4.2.1. Effects of partial pressures of methane and steam

The first notable kinetic study of the methane-steam reaction at high temperatures of interest for the SOFC (800–900°C) was by Bodrov et al. [47]. They carried out the steam reforming reaction on nickel foils which eliminated the effect of diffusion in pores. The same group also studied alumina-supported nickel catalysts [48], obtaining simple first-order methane kinetics. Much smaller activation energies in the latter case suggested that this simple behaviour was due to diffusion limitations.

More complex rate equations have been found for the reaction over nickel/alumina catalysts, involving partial pressures of all the components present. None describes the reaction rates both over wide temperature ranges and wide partial pressure ranges, leading to the suggestion [10] that more than one rate-determining step may apply, depending on the conditions.

It is perhaps surprising that few fundamental studies of steam reforming on SOFC anodes have been published. A summary of the most major published rate equations for nickel cermet anodes are shown in Table 1. It can be seen that there is considerable disagreement on the influence of steam partial pressures on reaction rate, although there is consensus that the order in methane is close to one.

4.2.2. Diffusion and temperature effects

There are wide variations in reported activation energies for the reforming reaction on anode cermets and therefore dispute as to the influence of diffusion in the anode of the SOFC. Achenbach [49] has suggested that mass transfer

effects are responsible for discrepancies in reforming reaction orders with respect to steam, and evidence for the existence of mass transfer limitation has been found in tests of planar 5×5 cm cells carried out by BG [50].

4.2.3. Other effects

Recent work in our laboratories suggest that the partial pressures of the products of the reforming reaction may significantly affect the reforming rate. This is particularly the case for hydrogen as shown in Fig. 6. This observation is contrary to the assumption almost universally made that only the reactants affect the rate but is consistent with some studies [51].

In addition to studying the reforming kinetics under cell operating conditions, we have carried out experiments using a plug flow tubular reactor [50]. Crushed half cells bearing nickel/zirconia anodes (60% Ni, 36 mm thickness) were employed and the influence of methane and steam partial pressures on the reforming rate in the range 2–40 and 10–70 kPa, respectively, was studied at 500, 800 and 1000°C. A maximum in the dependence of reforming rate on steam partial pressure was observed (Fig. 7) but this was at a higher steam partial pressure (28 kPa) than that observed by Yentekakis et al. [52] (~5 kPa) and was observed only at 1000°C. In addition, the position of this maximum was independent of methane partial pressure. Clearly this maximum could not have been due to the onset of carbon deposition because it was observed even at a steam:methane ratio of nearly 6, i.e. the conditions were well outside the thermodynamically-favoured region for carbon formation. It was hypothesised that competitive adsorption could be responsible for the observed behaviour. The rate equation deduced from our tests is also listed in Table 1. It includes three temperature dependent equilibrium constants k , k' and k'' .

In summary, whilst many kinetic studies are to be found in the literature and despite the fundamental importance to direct internally reforming SOFC system design of knowing the reforming rate at various conditions, very few systematic studies have been reported [53]. There is considerable discrepancy between the reported rate equations, although the consensus of opinion appears to be that the order in methane is close to one.

4.3. Mechanism of steam reforming in the SOFC

A mechanistic study by Lee et al. [54] suggested that the reforming reaction on nickel cermets follows a similar mechanism to conventional catalysts in that initial dissociative adsorption of hydrocarbon to a surface carbon species is followed by desorption of hydrogen and gasification of adsorbed carbon atoms by hydrogen or steam.

Yentekakis et al. [52] studied methane steam reforming rates on nickel-zirconia SOFC anodes in a mixed-flow reactor. For each temperature studied, a maximum in the reforming rate was observed which was attributed to competitive adsorption of steam and methane. However, the steam:-

methane ratios employed were sufficiently low at the maxima observed to constitute a carbon deposition threat on thermodynamic grounds, which casts some doubt on the reliability of the results.

4.4. Nickel cermet anodes under load

Eguchi et al. [55] are one of the few groups to study the influence of significant current density (up to around 200 mA/cm²) on the reforming reaction. Tubular cells were used, fed with 3:1 steam/methane mixture at 1000°C. The methane concentration thus varied from around 25% at the inlet to low concentrations at the outlet. An increase in methane conversion with current density was observed. A more recent study by the same workers [56] has shown that both steam and methane concentrations affect the $V-I$ curves of working cells. With methane the largest effects were noted at low current densities. The reason put forward is that at high concentrations of methane (low oxygen partial pressures in the anode) even a small current will affect the significantly local concentration of oxygen produced at the three phase boundary in the cell. This will enhance the concentration overpotential at the anode, thus depressing the $V-i$ curve. The effects are likely to be most severe at the inlet of an SOFC and the results confirm the idea that a practical stack should not be fed with pure methane, but with a partly pre-reformed fuel.

4.5. The composition of the nickel cermet anode

The anode of an SOFC is very different from a typical supported steam reforming catalyst, not only in the chemical nature of the support. The specific nickel area of state-of-the-art cermet anodes is orders of magnitude smaller, being around 0.35–3 m²/g [57] (cf. up to around 20 m²/g for steam reforming catalysts [18]). In addition, the physical structure of nickel cermets is typically a thin film. Nickel catalysts are most commonly employed as relatively large pellets leading to longer diffusion paths (low effectiveness factors). The effectiveness of thin films is however generally very high, and in practice state-of-the-art cermets have sufficient activity for the steam reforming of methane at the operating temperatures of YSZ SOFCs.

Reducing the nickel particle size in the anode significantly decreases the anode interface resistance, and will also improve the steam reforming activity. Rather than the traditional cermet preparative routes involving slurries, several groups are therefore exploring other preparative methods. Ogawa and others [58] have developed a vapour phase deposition technique for the preparation of porous YSZ to give a larger three phase boundary. Other workers in Japan [59] have patented a method of depositing Ni onto a substrate plate by dipping in NiCl₄ and drying. The substrate plate is porous YSZ of 100–200 μm thickness prepared by thermal spraying.

Table 1

Rate equations for reforming on SOFC cermets

Equation	Reference
$r_{\text{CH}_4} = \frac{kP_{\text{CH}_4}}{1 + a(P_{\text{H}_2\text{O}}/P_{\text{H}_2}) + bP_{\text{CO}}}$	Bodrov et al. [47] (on nickel films)
$r_{\text{CH}_4} = kP_{\text{CH}_4}P_{\text{H}_2\text{O}}^{-1.25}$	Lee et al. (see in [53])
$r_{\text{CH}_4} = kP_{\text{CH}_4}^{1.25}$	Parsons and Randall (see in [53])
$r_{\text{CH}_4} = kP_{\text{CH}_4}$	Belayev et al. (see in [53]), Achenbach and Riensche [49], Dicks et al. (Ni/Ceria cermet) (see in [53])
$r_{\text{CH}_4} = \frac{k(T)P_{\text{CH}_4}P_{\text{H}_2\text{O}}}{(1 + k'(T)P_{\text{CH}_4} + k''(T)P_{\text{H}_2\text{O}})^4}$	Dicks et al. (Ni/zirconia cermet) [50]
$r_{\text{CH}_4} = kP_{\text{CH}_4}^{1.3}P_{\text{H}_2\text{O}}^{-1.2}P_{\text{H}_2}^{0.4}$	Hishinuma et al. [51]
$r_{\text{CH}_4} = kP_{\text{CH}_4}^{0.85}P_{\text{H}_2\text{O}}^{-0.35}$	K. Ahmed et al. [81]

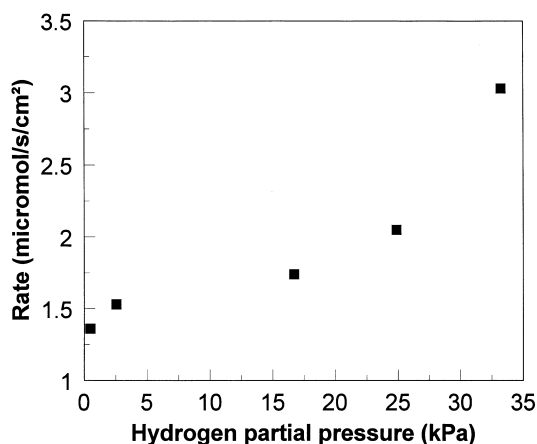


Fig. 6. Effect of hydrogen on the reforming rate on the SOFC anode.

One of the major problems with using nickel as the anode catalyst, however, is that it promotes the hydrocarbon cracking and CO decomposition reactions. If a catalyst was available that did not promote carbon forming reactions, then dry methane (or even natural gas) could in principle be fed to the fuel cell directly. For these reasons there is a growing search for new anode materials.

4.6. Alternative cermet anodes

Work at BG and elsewhere [60] have shown that substantial degradation of Ni–YSZ anodes can occur when used for steam reforming over long periods. We showed that over a 60%/40% Ni–YSZ anode with a steam/methane ratio of 2 the reforming activity fell to around 50% of its starting value over 1000 h. There is some dispute about the mechanism of the degradation [53], but several groups have doped the Ni–YSZ anode to enhance its electrochemical or steam reforming performance and stability. Eguchi [61] analysed the anodic polarisation conductivities of some different Ni–oxide cermets under various fuel atmospheres. They found that the anodic polarisation was influenced by the oxide component in the cermet as well as the metal.

As far as the zirconia phase is concerned, Westinghouse claimed a few years ago that small quantities of added ceria are beneficial [62]. Tokyo Gas [63] has also reported significant improvement in $V-I$ curves by doping Ni–ZrO₂ electrolyte with 10% Ceria. Mitsubishi Heavy Industries [64] have also patented a new anode material comprising Ni supported by a CeO₂/CeO₂–ZrO₂ mixture or CeO₂–YSZ mixture.

For the active and electronically conducting component, nickel is only one of several metals that will promote the reforming reactions. Other important ones are cobalt and some noble metals such as Pt, Rh and especially Ru. Ruthenium is particularly attractive since it exhibits a low activity towards the carbon forming reactions. Ru–YSZ cermets have been studied by Osaka Gas and others [65] and who have shown such materials also to have a high resistance to sintering whilst still possessing a high reforming activity. A

maximum power density of 4.55 W/cm² at 0.5 V and 3 A/cm² was obtained. More recently, Vernoux et al. [66] measured reforming activity (in a reactor) for Ru/TiO₂, Ru/LaCrO₃ and Ru/YSZ. The YSZ cermet gave the worse performance at low steam/methane ratios. In each case carbon deposition occurred at 800°C, but the CrO₃ and TiO₂ showed a lower propensity to carbon deposition at lower temperatures.

Cobalt-stabilised ZrO₂ cermets have been shown to have a high tolerance to sulphur [67] and Horita et al. [68] have shown that Fe, Ni, Pt, VC and La–Ca–CrO₃/YSZ anodes can be used for partial oxidation in the SOFC.

4.7. Ceramic conductors

A search was made some time ago by Steele et al. [69] for new conducting ceramic SOFC anodes. Mixed valence state titanates such as LiTi₂O₄, Mg_xTi_{3–x}O₅, CrTi₂O₅ and Niobium doped MgTi₂O₅, Mg₂TiO₄ and Sm₂TiO₇ were studied. Of these, the mixed niobium, magnesium pseudobrookites looked the most promising. Due to the instability of these materials over a wide oxygen partial pressure range, more work will be needed to determine the suitability of these materials for use as anodes in SOFCs.

4.8. Mixed ionic vs. pure electronic conductors

Recently mixed conducting oxides have been proposed for use as anodes for SOFCs. Their attraction, compared with simple metal cermets, is that electrochemical hydrogen oxidation reaction can occur over the whole surface of the ceramic conductor, and not just at the so-called triple point region between the electrolyte, electrode and gas as is the case for the metal electronic conductor. This is illustrated in Fig. 8. The large surface area for reaction is beneficial as it reduces the polarisation loss at the electrode [70]. The most widely studied mixed conductors are based on solid solutions in the Ti₂–ZrO₂–Y₂O₅ system. Examples are given in references [71–74]. Due to the presence of a variable valent

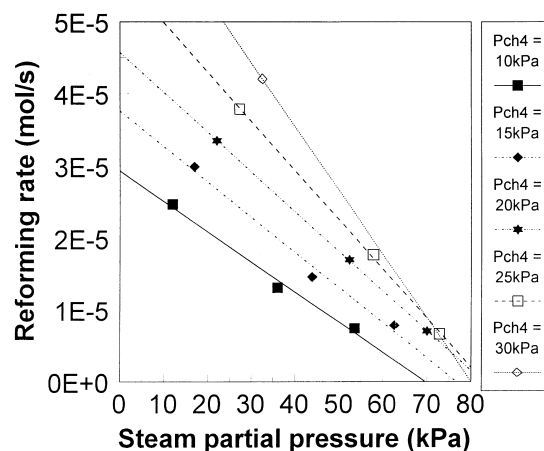


Fig. 7. Effect of steam partial pressure on the reforming rate on the SOFC anode.

titanium ion, it is possible that a catalytic process for the conversion of hydrocarbons can also occur on such materials, as in the Ni-cermet anode. Other mixed conductors that have been investigated include La–Ca–CrO₃/YSZ [75], YSZ with CeO₂ or TiO₂ additions, and TiO₂-doped YSZ [74]; and porous CeO/SmO (SDC) [76].

Finally, it may be possible to combine the advantages of a cermet with a mixed conducting material. Again, with the aim of increasing the three-phase boundary, catalytic mixed conducting layers may be inserted between the YSZ electrolyte and the electronically conducting cermet electrode. This approach has been investigated by groups at Northwestern and Pennsylvania Universities in the USA [77], who have deposited catalytic layers between the electrode and electrolyte on both anode and cathode sides, using, for example, yttria-stabilised zirconia-titania. Mitsubishi [78] have also demonstrated YSZ with a thin modified layer of mixed ionic and electronic conductor. (1, La/Ce; 2, Ce; 3, Sm/Ce and Pr).

5. Carbon deposition

There are many studies in the literature of carbon formation over nickel steam reforming catalysts [2,3]. Carbon can be formed through the thermal cracking of hydrocarbons or by the decomposition of CO. High molecular weight hydrocarbons are more likely to decompose to carbon than methane. Published data are available [2] that show the thermodynamic propensity of gas mixtures to deposit carbon on catalysts, assuming the gas is at equilibrium with respect to reactions Eq. (1) and Eq. (2). However, there are other factors that influence the likelihood of carbon formation. The nature of the solid catalyst is important both in terms of the metal and support. For example, carbon deposition is more likely over nickel than ruthenium catalysts, and acidic supports such as alumina tend to promote hydrocar-

bon cracking reactions more than alkaline supports such as MgO.

For the DIR–MCFC catalyst developed by BG, the limits of carbon formation by decomposition of methane or CO have been established by using a thermogravimetric technique. Similar experimental limits have been determined on Ni–YSZ SOFC anode material [50].

Commercial alumina-based steam reforming catalysts are doped with alkali to reduce the cracking activity of the acidic support. Modified supports have also been used to prevent carbon deposition in the SOFC. Anodes based on conductive CeO₂ have been found to be effective in oxidation of CH₄ without significant carbon formation [79], and recent results from Keele University [80] suggest that doping SOFC anodes with Mo may reduce carbon formation.

6. Conclusions

For the molten carbonate fuel cell, direct internal reforming catalysts are required which can operate in an alkaline environment. Catalysts have been now been developed by BG and others which have been proven under DIR–MCFC conditions for several thousands of hours.

In addition, protective shields have been devised which may reduce deactivation of DIR–MCFC catalyst by alkali.

DIR on the high temperature SOFC anode cermet is possible but the endothermic reaction produces thermal stresses which may limit the stack lifetime. Methods of reducing the temperature gradient include externally reforming or pre-reforming some of the fuel to reduce the duty on the anode. This also reduces the risk of carbon formation in the stack by removing the higher hydrocarbons. Risk of carbon deposition may also be reduced by modifying the ceramic component of existing cermets and by using metals such as ruthenium rather than nickel. Mixed conducting anodes also

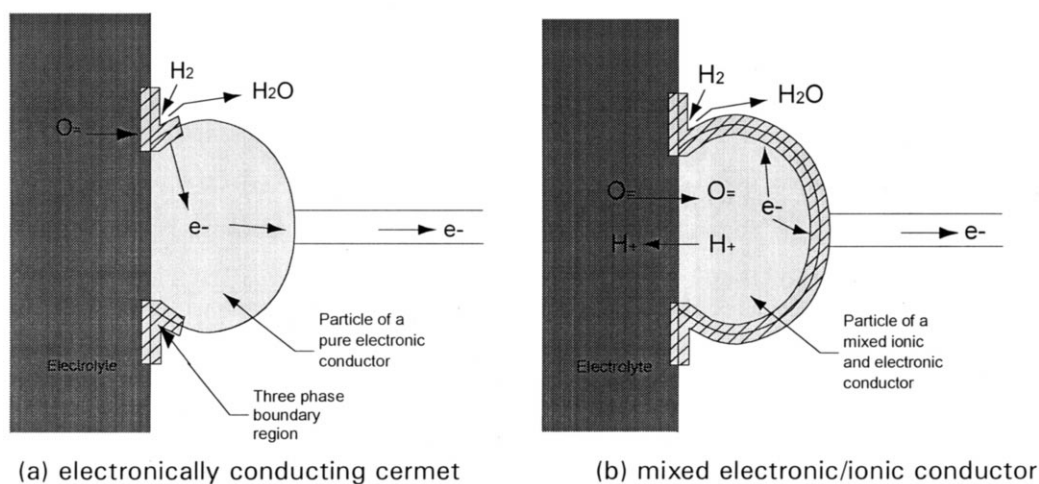


Fig. 8. Triple phase boundary in the SOFC anode.

offer a means of operating with lower steam/methane ratios, and increasing the catalytic activity. Such new anode materials may also be suitable for catalytic partial oxidation in the SOFC.

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