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Catalytic aspects of the steam reforming of hydrocarbons in internal reforming fuel cells

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Abstract

Steam reforming of hydrocarbons such as natural gas is an attractive method of producing the hydrogen fuel gas required by fuel cells. It may be carried out external to the fuel cell or internally. The two types of fuel cell in which internal reforming is most appropriate are the molten carbonate (MCFC), operating at ca. 650°C and the solid oxide (SOFC) which currently operates above 800°C. At such temperatures, the heat liberated by the electrochemical reactions within the cell can be utilised by the endothermic steam reforming reaction. This paper reviews some of the catalytic aspects of internal reforming in these two types of cell. In the MCFC the major catalyst issue is that of long term activity in the presence of a corrosive alkaline environment produced by the cell's electrolyte. In Europe, this is being addressed by British Gas and others, in a programme part-funded by the European Commission. In this programme, potential catalysts for the direct internal reforming MCFC were evaluated in 'out-of-cell' tests. This has led to the demonstration of a 1 kW proof-of-concept DIR-MCFC stack and the start of a European 'Advanced DIR-MCFC' project. For the SOFC, it has been shown that state-of-the-art nickel cermet anodes can provide sufficient activity for steam reforming without the need for additional catalyst. However, anode degradation may occur when steam reforming is carried out for long periods. New anode materials could therefore offer significant benefits. © 1997 Elsevier Science B.V.

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1. Introduction

Hydrogen is the preferred feedstock for use in the present generation of fuel cells. The main reason is its high electrochemical reactivity compared with the more common fossil fuels, such as hydrocarbons, alcohols or coal, from which it may be derived [1].

Steam reforming is a well established process for producing hydrogen or synthesis gas from natural gas or other hydrocarbons. The overall reaction is highly endothermic and is normally carried out at temperatures above 500°C, typically around 700–800°C in the presence of a suitable catalyst. To be of use in fuel cell systems, heat needs to be available to drive the steam reforming reaction. One method of achieving this, for example, is to feed the exhaust gases from the anode and cathode into a burner where excess fuel from the anode is combusted. The heat generated in the burner can then be used to preheat steam and fuel and provide the heat needed in the reformer. Heat exchange reformers have been proposed by a number of developers for this purpose, and a leading example is the Topsoe Heat Exchange reformer [2].

A more elegant method of providing heat for reforming in fuel cell systems is to carry out the endothermic reactions inside the fuel cell stack. The

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molten carbonate fuel cell (MCFC) and the solid oxide fuel cell (SOFC) both operate at high enough temperatures for this to be possible. Internal reforming lowers the requirement for cell cooling and, by eliminating the need for an external reformer, capital costs are also reduced.

1.1. *Steam reforming*

Steam reforming is a mature technology, practised industrially on a large scale for hydrogen production and several detailed reviews of the technology have been published [3–5]. The reforming reaction (1) and associated water-gas shift reaction (2) are carried out over a supported nickel catalyst at elevated temperatures, typically above 500°C.

$$CH_4 + H_2O = CO + 3H_2 \quad (\Delta H^0 = 206.2\,\mathrm{kJ\,mol^{-1}}) \tag{1}$$

$$CO + H_2O = CO_2 + H_2 \quad (\Delta H^0 = 41.1\,\mathrm{kJ\,mol^{-1}}) \tag{2}$$

The higher hydrocarbons in natural gas also react with steam in a similar fashion:

$$C_nH_m + nH_2O = nCO + (n + m/2)H_2 + \text{heat} \tag{3}$$

Reactions (1) and (2) are reversible and are normally at equilibrium as the reaction rates are very fast. The composition of the product gas from a conventional reformer reactor is therefore governed by thermodynamics. Steam is normally added well in excess of the stoichiometric requirement of reaction (1) so that the equilibrium of reaction (2) moves towards more CO_2 production rather than CO. This is to avoid carbon deposition via the Boudouard reaction (4) which is also catalysed by nickel.

$$2CO = CO_2 + C \quad (\Delta H^0 = 86.2\,\mathrm{kJ\,mol^{-1}}) \tag{4}$$

Steam may be replaced completely (or in part) by CO_2 which gives a more favourable H_2/CO ratio for some applications:

$$CH_4 + CO_2 = 2CO + 2H_2 \quad (\Delta H^0 = 247\,\mathrm{kJ\,mol^{-1}}) \tag{5}$$

The equilibrium constants for all of these reactions are well known and it is possible to predict the product gas composition of a reformer knowing the atomic ratios of H : C and O : C present, as well as the pressure and temperature. Usually the predicted equilibrium outlet composition is close to the measured values, and small differences are expressed as an "approach to equilibrium temperature".

Methane may also be converted to a hydrogen rich gas via partial oxidation which may be catalysed or non-catalysed. Partial oxidation may be expressed in different ways; if methane can be oxidised to hydrogen and CO_2 the reaction is exothermic:

$$CH_4 + O_2 = CO_2 + 2H_2 \quad (\Delta H^0 = -320\,\mathrm{kJ\,mol^{-1}}) \tag{6}$$

Several metals have been found to catalyse reactions (1)–(6), but nickel is generally preferred on cost grounds. In commercial steam reforming catalysts, the nickel is supported on a refractory oxide. The choice of support is governed by the surface area required, as well as the need for stability in the operating environment. Various modifications of alumina are frequently used. The most stable form of alumina is corundum, or α-alumina, and this is an ideal support for high temperature steam reforming applications where a high specific activity is not required. However, for greater activity the catalyst can be prepared by a co-precipitation method. The nickel and alumina are co-precipitated as hydroxy-carbonates by addition of alkali to an aqueous solution of their salts. The precipitate is subsequently separated by filtration, washed, dried and then calcined to decompose the precursor to nickel oxide and alumina. Unfortunately this method of preparation leads to the formation of γ-alumina which is thermodynamically less stable than the α-form. Under high partial pressures of steam at elevated temperatures, such as are present under steam reforming conditions, the γ-alumina converts to α-alumina over a period of time. Such 'hydrothermal sintering' results in a substantial change in the microstructure of the catalyst and leads to degradation of the catalyst activity. Many methods of producing stable supports have been devised over the past 30 years and commercial catalysts frequently contain mixtures of alumina, magnesia, zirconia and other ceramic oxides.

The physical form of steam reforming catalysts has also evolved over many years to maximise the activity and rate of heat transfer within the reformer reactor. The catalyst pellet size is a compromise between ensuring good packing, mechanical stability and low pressure drop. The pressure drop is in turn governed by the vessel size and mass velocity for which the reactor is designed.

1.2. Kinetics and mechanisms

Research over many years has shown that over nickel the steam reforming of hydrocarbons occurs via a surface carbon species. Chemisorption of hydrocarbons on metals involves the direct breaking of a C–H bond. 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 [6]:

$$CH_4 = CH_3^* \rightarrow CH_2^* \rightarrow CH^* = CH^* \quad (7)$$

The methane adsorption has generally been thought to be the rate determining step in methane steam reforming, consistent with the generally assumed first order dependency of the rate in methane [7]. Workers in the 1970s fitted experimental data with nickel catalysts to more complex rate expressions. Quach and Rouleau for example in 1975 [8] measured rates in an CSTR and found that for Ni/α-alumina:

$$r = \frac{k[CH_4][H_2O]^2}{1 - a[CH_4](1 - K/K)}, \quad (8)$$

where [x] is the partial pressure of species x; k and a are constants, K is the equilibrium constant for reaction (1) and K'=K calculated from non-equilibrium concentrations.

A wide variety of such expressions have been reported to hold over limited temperature and pressure ranges [9] although most work has been carried out between 500°C and 900°C. More recently Froment et al. [10] have derived a single expression describing the rate of reaction (1):

$$r = \frac{kpCH_4pH_2O(1 - Q_R/K_p)/pH_2^{2.5}}{1 + KCOpCO + KH_2pH_2 + KCH_4pCH_4 + KH_2O(pH_2O/pH_2)}, \quad (9)$$

where Q_R and K_p are the reaction quotient and the equilibrium constant, respectively for reaction (1). In addition to K_p, Eq. (9) also contains four other temperature dependent equilibrium constants KCO, KH_2, KCH_4, KH_2O. Despite its sophistication, Eq. (9) could not adequately describe the decrease in rate when steam was replaced by carbon dioxide [11] (i.e., Eq. (5)). Apparently the mechanism of steam reforming cannot be represented by a single rate determining step (rds) for a wide range of conditions. It is perhaps also unreasonable to assume that the mechanism for steam reforming over nickel will be the same for other catalytic metals. Ross, for example showed that a different rate expression for reaction (1) holds over Ru/Al_2O_3 [12].

1.3. Carbon deposition

For a given steam/methane ratio it is possible to predict the thermodynamic likelihood of carbon deposition via reaction (4) from an equilibrium gas mixture containing carbon oxides, hydrogen, steam and methane. However, it has been well established that the thermodynamic minimum steam/methane ratio for carbon deposition over nickel catalysts via reaction (4) is lower than predicted from the thermodynamic data for graphite formation. On nickel it has been fairly well established that the key reactions occur over a surface layer of nickel atoms. If such layers are allowed to build up (e.g., because of low steam partial pressure) a filament or whisker of carbon can start to grow attached to a nickel crystallite. Such carbon filaments can generate massive forces within catalyst pellets and once started can lead to rapid catalyst breakdown, and the blocking of reactor tubes. Fig. 1 shows carbon filaments formed on a catalyst used for internal reforming in the MCFC following failure of the steam supply to the cell.

Carbon may also be formed by thermal cracking of hydrocarbons in the absence of air:

$$CH_4 = C + 2H_2 \quad (\Delta H^0 = 75\,kJ\,mol^{-1}) \quad (10)$$

$$C_nH_m = nC + \tfrac{1}{2}mH_2 \quad (11)$$

Reactions (10) and (11) tend to lead to a surface pyrolytic carbon which can encapsulate the nickel particles. Such reactions have the greatest risk of occurring at the inlet of a reformer where there is almost no hydrogen present. At this point the likelihood of carbon formation is governed not so much by

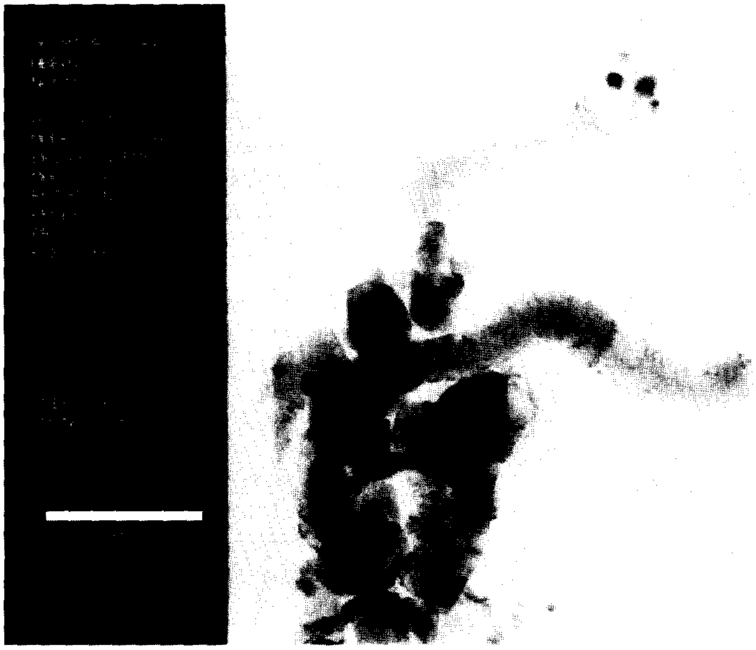

Fig. 1. Carbon deposition on a supported nickel DIR-MCFC catalyst.

equilibrium considerations but by the relative kinetics of the carbon forming and carbon removal (gasification) reactions.

Higher hydrocarbons have a greater propensity for carbon deposition than methane. Thermal or steam cracking of hydrocarbons can occur above 600–650°C even in the absence of nickel catalysts. The cracking leads to olefins followed by a carbonaceous polymer which can dehydrogenate to produce coke. For this reason, it is common to carry out some pre-reforming of hydrocarbon feeds, such as natural gas, to remove the C_2+ hydrocarbons before the gas is fed to the main reformer. Pre-reforming can be carried out adiabatically at relatively low temperatures where the carbon deposition reactions do not occur. Typically pre-reforming is done in the range 250–500°C [13].

The tendency for carbon deposition can be reduced, for example by the addition of alkali to nickel catalysts. It has also been found that controlled passivation of catalyst with sulphur can reduce carbon formation and this is practised in the Topsoe SPARG process [14]. Fortunately carbon filaments do not appear to form on precious metals such as ruthenium or rhodium which are also catalytically active for steam reforming.

2. Internal reforming

There are two basic internal reforming concepts, and these are usually referred to as direct (DIR) and indirect (IIR) internal reforming. In the case of DIR, reforming takes place either directly on the anode or within the fuel channel of the cell. Heat and steam are supplied directly from the electrochemical reaction. The electrochemical reaction also helps to drive the reforming reaction to completion by removing the hydrogen as it is formed. DIR results in high conversion and high cell efficiencies, even at the relatively low temperature of the MCFC. As far as IIR is concerned, the reforming reaction takes place in a compartment which is in close thermal contact with the cell. This gives the advantage of good heat transfer from the cell but without the hydrogen and steam synergy between the anode electrochemical reaction and the reforming reaction.

2.1. *Advantages and disadvantages of internal reforming*

In contrast to both the steam and CO_2 reforming reactions (1) and (5), 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 CH_4 [15]. The overall heat production is about half the heat consumed by the internal steam reforming. Hence the cooling required by the cell, which is usually achieved by flowing excess gas through the cathode, will be much smaller. Application of internal reforming offers several further advantages compared with external reforming:

1. System cost is reduced because the separate steam reformer unit is not needed.
2. With DIR less steam is required (the anode reaction produces steam).
3. There is a more evenly distributed load of hydrogen in a DIR cell which may result in a more uniform temperature distribution.
4. There is a higher methane conversion.

There are however some disadvantages:

1. It may be necessary to incorporate catalyst, which may require modification of stack hardware.
2. Catalyst can become deactivated. Conventional catalysts may be poisoned by impurities (e.g., sulphur compounds) in the feed fuel, or by sintering of the active metal and/or support. The alkali present in the electrolyte of the MCFC can contribute to additional catalyst deactivation.
3. Although the reforming and electrochemical reactions may be synergistic, integration of the two functions may reduce the flexibility of operation of the fuel cell. This is likely to be more of a problem with DIR compared with IIR.

3. Internal reforming in the MCFC

The concept of the MCFC dates back to the 1940s and the first cells were demonstrated by Broers and Ketelaar in the late 1950s. Development in materials science over the last few decades has added considerably to understanding of the technology. From this the development of stacks has reached the early demonstration stage of pre-commercial systems. To move the technology from the laboratory into the market place, major MCFC projects have been established in several countries. Work on internal reforming MCFCs is currently being undertaken, notably in Europe, the United States and Japan.

In Europe there are two main groups of organisations involved. The first is led by BCN (Dutch Fuel Cell Corporation) and ECN (the Dutch Energy Research Foundation). Over the past few years British Gas and CNR (Consiglio Nazionale delle Ricerche, Messina, Italy) have been collaborating with the Dutch organisations to develop DIR-MCFC technology. This collaboration led a demonstration in 1993 of a 1 kW proof-of-concept stack, and novel concepts for heat management in MCFC systems [16]. Additional work was provided by the centre for advanced ceramics (CKKO) at the University of Twente. At the beginning of 1996 a major European Union supported programme was started to build on these developments. The principal partners in this 'Advanced DIR-MCFC development' are BCN, ECN, British Gas, Gaz de France and Sydkraft (Sweden) [17].

Germany is the focus of the other major European MCFC work. In this case the group of companies (ARGE) is led by MTU Motoren-und-Turbinen Union Friedrichshafen, with collaboration from Ruhrgas, RWE, Elkraft (Denmark) and Haldor Topsoe (Denmark).

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 250–2 MW scale. ERC utilise internal reforming stacks whereas MC-power are currently focused on using external reforming stacks in conjunction with plate reformers.

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

State-of-the art MCFCs operate at temperatures around 923 K. The electrolyte is usually a mixture of 62 mol% Li_2CO_3 and 38 mol% K_2CO_3 [18], constrained with a porous 'tile' of $LiAlO_2$. The anode is made from porous nickel, stabilised with addition of other metallic elements. The operating temperature is constrained by the need to ensure a high ionic conductivity of the electrolyte and low polarisation of the electrodes while avoiding the corrosion of metallic components which occurs at higher temperatures.

For two reasons direct internal reforming provides the biggest challenge to MCFC developers. Firstly the catalyst needs to be able to operate for extended periods in the presence of a corrosive alkali, originating from the electrolyte. Small amounts of the electrolyte gradually migrate towards the catalyst during operation, either by liquid creep or via a vapour phase mechanism. Secondly, the catalyst needs to provide sufficient activity so that the rate of the reforming reaction is matched to the rate of the electrochemical reaction. This is to ensure that temperature variations across the cell are kept to a minimum, to reduce thermal stress, and thereby contribute towards a long stack life. A more uniform temperature distribution across the stack may also be achieved through the recycle of either anode gas, or cathode gas, or indeed both.

3.1. *Mechanisms of internal reforming in the MCFC*

Fig. 2 shows a schematic representation of a repeating unit in an MCFC stack. Hydrogen in the fuel reacts with carbonate ions from the electrolyte producing electrons which are the source of the electric power from the cell:

$$H_2 + CO_3^{=} = CO_2 + H_2 + 2e^- \qquad (12)$$

The anode consists of porous nickel, strengthened and stabilised by oxides formed, for example, by the addition of Cr. The porous structure of the anode becomes partly filled with the electrolyte which is usually a mixture of molten lithium and potassium carbonates. Selman [19] in a review of processes occurring in the MCFC points to considerable agreement about the kinetics of the anode reaction, and minor disagreements about the mechanism. There is little doubt that hydrogen is first dissociatively adsorbed on the electrode (nickel) surface. Sammells [20] then proposed that hydrogen reacts in two on-electron transfer reactions in series, whereas Jewulshki and Suski [21] have proposed two one-electron transfer reactions in parallel thus:

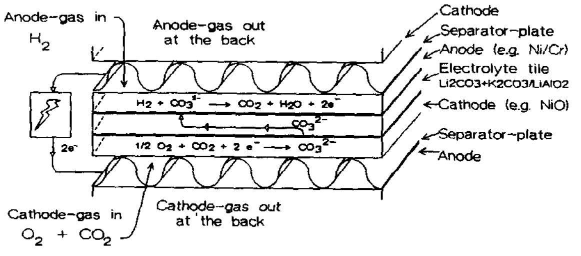

Fig. 2. Schematic representation of a repeating unit in an MCFC stack.

$$H_2 + 2M = 2M{-}H \qquad (13)$$

$$2(M{-}H + CO_3^{=} \rightarrow OH^- + CO_2 + M + e^-) \quad (\text{rds}) \qquad (14)$$

$$2OH^- + CO_2 = H_2O + CO_3^{=} \qquad (15)$$

The surface reaction of the adsorbed hydrogen with the carbonate ions is probably the rate determining step of the anode electrochemical reaction. Nishina et al. [22] have studied hydrogen oxidation using linear potential sweep, AC impedance and cyclic voltammetry on Au, Ni and Cu electrodes. These all suggest that the above mechanism is the most likely. It is worth remarking however that hydrogen adsorption can also take place below the molten carbonate. Hydrogen can diffuse through the nickel particles as well as through the carbonate.

3.2. *Internal reforming catalysts*

At the operating temperature of the MCFC, it is necessary to use a nickel catalyst to promote the internal reforming reaction. It has been demonstrated for many years that conventional supported nickel catalysts provide sufficiently high conversion of methane. At atmospheric pressure and 650°C the degradation rate using sulphur-free methane is also very low. However additional issues are important in an MCFC:

1. 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) could be used. There is a need to establish if they can be internally reformed and several potential fuels have now been tested in laboratory cells and stacks. Many fuels (including natural gas) also contain impurities (e.g., sulphur) which are harmful for the MCFC anode and/or the

reforming catalyst. There is a need to determine the effects of such contaminants and validate methods of their removal for real MCFC systems.
2. The strongly endothermic reforming reaction causes a pronounced dip in the temperature profile of an internal reforming cell. This has ramifications for the DIR system as it can impose considerable thermal stress on a full scale stack. Options to decrease this effect include recycling the anode gas and/or the cathode, and to change the flow configuration of the stack.
3. With DIR, alkali from the electrolyte has been shown to significantly deactivate catalysts to the extent that it is a major factor affecting cell lifetime and hence economic viability of IR stacks. Alkali can affect the sintering of both the nickel particles and the support [23].

The activities of catalyst developers has therefore been focused in recent years, not on IIR, for which a number of commercial materials are available, but in developing DIR catalysts.

3.3. *Effects of alkali*

Development of direct internal reforming catalysts has mainly concentrated in the past on nickel supported on alkali-resistant materials such as MgO [24–26] and $LiAlO_2$, many of which have been shown to be successful for internal reforming of methane. However, Berger et al. [27] 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.

As mentioned above, potassium is well known as a promoter in steam reforming catalysts. Recent quantum mechanical calculations [23] 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. The observed fall in activity was attributed to a surface carbidic species which is increased by the addition of alkali. Rostrup Nielsen [23] 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 [28] to the effect of alkali on the support.

It has been shown that alkali will be more easily absorbed by more acidic supports such as Al_2O_3 than basic ones such as MgO [29]. MgO catalysts have been investigated in some detail by Cavallaro et al. [25] who have shown that in a DIR-MCFC test lasting 860 h, alkali deactivates the catalyst by a pore blocking mechanism. The fresh catalyst used in the test contained no K or Li but on discharge from the cell test contained between 0.59 to 1.4 wt% Li and from 5.2 to 8.7 wt% K. A glassy layer of KOH was formed which covered the whole of the external surface of the pellets, preventing access to the active sites of the catalyst, thereby inhibiting methane conversion.

3.4. *Development of protective shields*

In the DIR-MCFC there is belief that it may be possible to extend the lifetime 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 [30]. More recent applications of the nickel foil concept have been proposed by workers at Sanyo [31]. Hitachi have proposed the use of a sintered nickel fibre or a porous ceramic [32]. 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 [33]. Toshiba claim that B_4C, HfN, ZrO_2 can repel alkali but can be made porous to H_2 and H_2O [34].

3.5. *Development of alternative catalyst*

Although work continues on nickel-based DIR-MCFC catalysts [35], precious metal catalysts have recently been investigated, particularly for the internal reforming of light hydrocarbons such as LNG, LPG naphtha and kerosene. Tonen have proposed and tested various supported metals of which ruthenium and rhodium were found to be especially stable [36,37]. In conjunction with Sanyo, Tonen have shown that deactivation of Ru/ZrO_2 catalyst over a period of 2700 h is very small [38].

4. DIR-MCFC catalyst research

Work has been carried out by British Gas to identify catalysts that are capable of extended operation for the direct internal reforming of natural gas [16]. Several catalyst types have been examined over the past few years: commercial nickel-based steam reforming catalysts, usually prepared by coprecipitation or impregnation, and development catalysts prepared by a variety of routes. The development catalysts were usually nickel or ruthenium based, and the supports comprised γ-Al_2O_3, SiO_2, or MgO with various promoters. In addition to material prepared by British Gas, some development catalysts were also supplied by CNR–TAE and CKKO. Some of the most successful materials were prepared by homogeneous precipitation and deposition precipitation [27].

To assess catalyst resistance to deactivation by alkali, a small-scale 'out-of-cell' (as opposed to an 'in-cell' fuel cell) test was developed to mimic conditions encountered within the DIR-MCFC. Following the tests, the chemical and physical properties of the catalyst samples were determined. The tests have been described in detail elsewhere [16] and the following provides a summary of the most important findings.

4.1. *'Out-of-cell' tests*

A series of catalysts in the form of 1/8″ (3.2 mm) cylindrical pellets or small granules were mixed with α-alumina pellets doped with potassium and lithium carbonates (in the proportions used in an MCFC electrolyte) and loaded into a vertical stainless steel reactor tube. The catalysts were reduced in a stream of hydrogen at 650°C and 25 psig pressure for 24 h prior to admitting the reactants for steam reforming. Then a stream of reactants, comprising one part desulphurised natural gas and two parts of steam, were passed over the catalyst bed at the same temperature. Reforming was carried out with a reactor inlet temperature of 650°C and at a pressure of 25 psig. The gas hourly space velocity (GHSV) used was $530\,h^{-1}$ for the carbonate tests and $830\,h^{-1}$ for the non-carbonate tests. The duration of the tests varied from 0 to 2500 h, but the majority were carried out for 1000 h. These experiments were carried out both in the presence and absence of molten carbonate in order to determine the effect of the carbonate on each catalyst.

Table 1

Typical gas compositions (mol%) of out-of-cell tests steam reforming tests

	Feed gas	Measured product
H_2	0.05	67.1
CO_2	0.6	11.6
N_2	1.9	1.1
CO	0.0	8.5
CH_4	93.2	11.7
C_2H_6	3.5	n.d.

The temperature profile of the catalyst bed was recorded each day, and the feed and product gas compositions were determined at regular intervals (see Table 1). During the tests, the extent to which a catalyst experiences deactivation can be gauged from the shape of the 'temperature profile' and the recorded product gas analyses. The shape and depth of the endotherm is representative of the operating conditions of the test, and its position is indicative of the catalyst performance.

Examples of profiles recorded from a Ni/γ-alumina catalyst performing well under MCFC conditions are shown in Fig. 3. 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. However, a catalyst experiencing severe deactivation produces the profiles shown in Fig. 4. This example was for a Ni/MgO catalyst, and in this

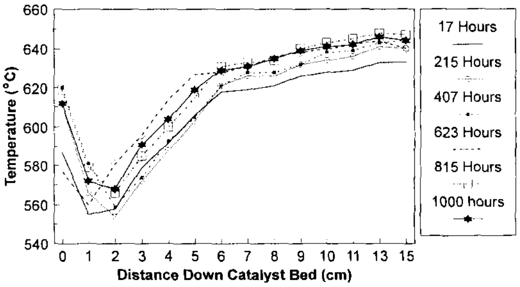

Fig. 3. Temperature profiles of 'out-of-cell' test for Ni/Al_2O_3.

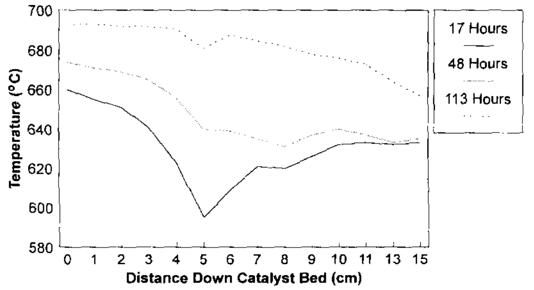

Fig. 4. Temperature profiles of 'out-of-cell' test for Ni/MgO catalyst.

case the endotherm appears progressively shallower and its position moves further down the bed with time.

4.2. *Post test analysis*

Upon completion of each test, the catalyst was cooled to ambient temperature in flowing hydrogen and then passivated by admitting carbon dioxide. The catalysts were discharged from the top, middle and bottom of the bed so as to measure any changes along its length. The catalyst samples were then submitted to a number of routine chemical and physical analyses. Further to these analyses, some catalyst samples were investigated using surface science techniques – Auger electron spectroscopy (AES), transmission electron microscopy coupled with energy dispersive X-ray analysis (TEM/EDX), X-ray photoelectron spectroscopy (XPS) and laser ion induced mass analysis (LIMA).

TEM/EDX measurements on catalysts discharged from the out-of-cell tests have shown, in the case of some γ-alumina supported catalysts, that potassium contamination is associated with the support rather than the nickel after 50 h of use. It has been postulated that the potassium bonds to the surface tetrahedral Al^{3+} ions, thus preventing potassium from covering or possibly bonding with the nickel [39].

In contrast to the nickel/γ-alumina catalyst, a nickel/magnesia catalyst used in out-of-cell tests (see Fig. 4) experienced sever deactivation which can be linked to the collapse of the support. After 200 h the total surface area, measured by nitrogen adsorption, dropped from 30 to 1 $m^2 g^{-1}$, and a substantial decrease in the nickel surface area also occurred. In this case AES measurements indicated that the potassium is associated with both the nickel and the support. As the probing depth of AES is small, the results indicate that the depth of covering of the magnesia is not large [40].

Results from ECN and British Gas show that out-of-cell tests produces a more severe environment than in-cell tests. The levels of potassium deposited on catalysts from out of cell tests were in some cases three times greater than those from equivalent in-cell tests. However, routine analyses of the discharged catalysts showed no significant differences between the physical properties of the samples. The results show that the out-of-cell test produces a realistic and stringent 'screening' process for fuel cell catalysts.

4.3. *In-cell tests*

Candidate catalysts were selected on the basis of the out-of-cell tests for further testing in 'bench scale' 10×10 cm fuel cells. These were undertaken by ECN within the JOULE projects, but characterisation of the catalysts has been undertaken by British Gas. Typical test conditions used in the in-cell tests are given in Table 2.

Tests of 1000 h duration at temperatures of 600°C, 650°C and 700°C have shown that at lower temperatures the catalyst exhibits slower deactivation than at higher temperatures. This is in agreement with work recently carried out by workers at Mitsubishi [41] and confirms the earlier findings by Baker et al. [42].

An additional series of tests (using a British Gas development catalyst) carried out for periods up to 5000+ h has shown that the nickel crystallite size increased from an initial value of below 50 Å up to 800 Å. In addition, the alkali uptake increased to a level of several percent. Nevertheless, measurements have shown that the catalyst still retained a large activity level for steam reforming.

Fig. 5 shows the deactivation of three types of catalyst that were tested for 1000 h bench scale DIR-MCFC tests. Catalyst A was a commercial nickel/calcium aluminate high temperature steam reforming catalyst, B was a nickel/γ-alumina catalyst prepared by a deposition precipitation method and catalyst C was a co-precipitated nickel/γ-alumina stabilised by a proprietary British Gas method [43]. In each case the form of the catalyst was 3.2 mm equant cylindrical pellets. The results of such tests

Table 2
Bench-scale standard test conditions

	Non-reforming	Direct internal reforming
Fuel		
Dry composition $CH_4/H_2/CO_2$	0/80/20 (%)	97/3/0 (%)
H_2 utilisation at 150 mA/cm^2	75 (%)	75 (%)
Wet composition $CH_4/H_2/CO_2/H_2O$	0/64/16/20 (%)	33/1/0/66 (%)
Oxidant		
Dry compsotion air/CO_2	70/30 (%)	70/30 (%)
CO_2 utilisation at 150 mA/cm^2	50 (%)	50 (%)
Wet composition air/CO_2/H_2O	66.1/28.3/5.6 (%)	66.1/28.3/5.6 (%)
Typical open circuit voltage	1.10 V	1.06 V
Typical cell voltage at 150 mA/cm^2	0.8 V	0.8 V

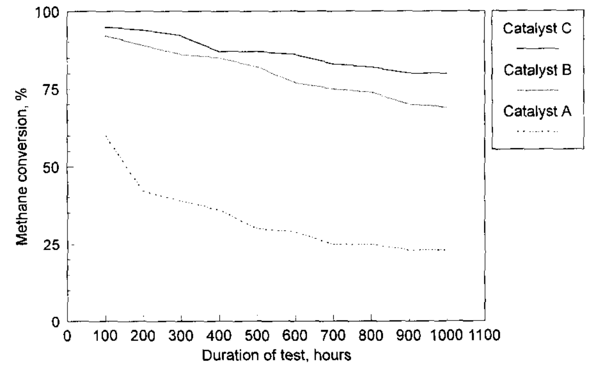

Fig. 5. Performance of three types of DIR-MCFC catalysts in cell tests (from [16]).

show that catalyst formulations have been established that have lifetimes of several thousand hours. Following these bench scale tests, the DIR concept has been demonstrated at the 1 kW scale [16] and plans are in hand to scale up this technology in a new collaborative project [17].

5. Internal reforming in the SOFC

Several groups have shown that in the SOFC operating above 800°C, direct internal reforming can take place on the nickel cermet anode. Unlike the MCFC, an additional catalyst is not required. However if the anode is to be used as the catalyst, it must meet several requirements:

1. Stability under operating conditions.
2. High electronic conductivity.
3. Minimum chemical reactivity and diffusivity with other cell components
4. Thermal expansion similar to the electrolyte.
5. Stable pore structure.
6. Stable reactivity for steam reforming and electrocatalysis.

Ni/ZrO_2 has been adopted by most SOFC groups as the state-of-the art anode. It is excellent for the oxidation of H_2, and has a good match of properties with the ZrO_2 electrolyte. Calcia doped ceria–nickel cermet has also been investigated. It has the advantage that ceria is a mixed ionic and electronic conductor at high temperatures. Below about 700°C ceria is predominantly an ion conductor and is becoming more important for use in low or 'intermediate temperature' SOFCs. There is considerable interest in the use of other materials, particularly mixed oxides rather than cermets, as anodes for the SOFC. Fagg et al. [44] for example have examined zirconia doped with titania or niobia and Steiner Middleton and Steele have studied various ternary titanates [45]. So far, however, no materials have showed performance or endurance levels better than Ni/ZrO_2 cermet.

The same principal advantages arising from internal reforming in the MCFC are also realised in the SOFC. Although there is no deactivation of catalyst due to the presence of alkali, the activity of the anode is likely to decrease due to the usual routes of sintering or poisoning from contaminants in the feed. Westinghouse have demonstrated that sulphur poisons the anode, but that degradation can recover when sulphur in the feed is removed [46,47]. Moreover, early work by Westinghouse suggested that carbon deposition was a major concern, particularly from the decomposition of higher hydrocarbons in the feed. For this reason many workers recognise that some degree of pre-reforming (or external reforming) of the fuel is required for SOFC systems. Westinghouse currently carry out some 60% reforming outside the cell and 40% internal reforming.

5.1. *Kinetics of internal reforming in the SOFC*

The kinetics of methane reforming over nickel cermet have been fairly well established, at least at high temperatures [9,48–50]. Lee et al. [9] have carried out the most detailed work so far on anode materials for the SOFC. Ni/ZrO_2 cermets with Ni 50–80% (w/w), were prepared with a range of porosities (14–66%). Reaction rates measured in a Carberry reactor led to the conclusion that reforming rate increased with H_2O/C ratio and with temperature. Lee concluded that reforming is first order in methane and -1.25 in steam. Achenbach has recently showed [50] that for a 80/20 Ni–YSZ anode, over the range 700–940°C the rate is first order in CH_4 and zero in steam, and Belyaev et al. [51] have shown that the same kinetic expression holds for a mixed Ni–(5 wt%)ZrO_2–(2 wt%)CeO_2 anode.

5.2. *SOFC work at British Gas*

Recent work at British Gas [49] has demonstrated, for Ni/ceria anodes, the rate of steam reforming is given by

$$r = kp\mathrm{CH_4} \qquad (16)$$

when $1.6\,\mathrm{kPa} < p\mathrm{CH_4} < 18\,\mathrm{kPa}$ and $5.4\,\mathrm{kPa} < p\mathrm{H_2O} < 39\,\mathrm{kPa}$.

In cells running at low current densities (below 100 mA/cm^2) the reforming reaction is not affected by the cell operation and the measured cell V/I curve running on methane/steam is close to theoretical. Achenbach [50] has suggested that some previously reported dependencies of reaction rate on the steam/methane ratio may be due to mass transfer effects, although no evidence has been found for this in the present studies. Tests have, however, showed that there are significant differences in reforming activity over the anodes of cells having different compositions and obtained from different sources.

Operation of the Ni/ceria cermet anode in a 98% hydrogen 2% steam environment resulted in very little change in the microstructure of the anode over a period of 50 h. Increasing the steam partial pressure, however, results in some sintering of nickel in the anode. High steam concentrations are known to degrade anodes and recent work by British Gas has shown that operation of a cell on steam/methane, rather than hydrogen, results in an increase in sintering of the nickel.

Tests carried out on single cells fed with desulphurised natural gas and steam mixtures have shown that there is a greater tendency towards carbon deposition compared with cells run on pure methane. In a fully engineered SOFC internal reforming system it is likely that the fuel gas will be a complex mixture. To ensure that a system self-sufficient in water it is desirable, for example, to provide steam for the reaction by recirculating the anode exhaust gas [46]. With such an arrangement CO_2 and some hydrogen will also be fed to the anode which should reduce the possibility of carbon deposition. However, since the composition of natural gas can vary widely according to the source, great care will be needed in designing gas clean-up and processing for such systems to ensure that carbon deposition does not occur.

6. Direct use of natural gas in fuel cells

Internal reforming places constraints on the design of systems both for the MCFC and SOFC. The complete oxidation of methane to CO_2 and H_2O is a highly exothermic reaction (ΔH^0=802.5 kJ mol^{-1}) and the entropy change is very small (ΔS^0=6 kJ mol^{-1}). Thus if it were possible to combust methane directly in a fuel cell (without any intermediate reactions) the thermodynamic efficiency would be close to 100%. The fuel would not react via the steam reforming route. Attempts to run fuel cells directly on methane were attempted in 1960s with mixed success. Subsequently, progress has been made by several workers [1]. Some of the best performances reported so far with the SOFC running on dry methane are those of Mogensen et al. [52] who have operated the yttira-stabilised zirconia SOFC at 800–1000°C using anodes made of mixed ion-conducting oxides of ceria–gadolinia. They claim to have measured rates of methane oxidation which could make their fuel cell a competitive power generator.

7. Conclusions

Catalysis plays an important role in the internal reforming molten carbonate and solid oxide fuel cells. The requirements for each are very different and in several countries organisations are actively developing both types of fuel cell. The direct internal reforming MCFC offers the greatest challenges for a steam reforming catalyst, but work at British Gas and elsewhere has shown that lifetimes of several thousand hours may be expected in practical systems. In the case of the SOFC it is possible to directly reform hydrocarbons on the anode without the need for an additional catalyst. However, even when natural gas is used as fuel some degree of pre-reforming will probably be required to remove the higher hydrocabons. This will ensure that the risk of carbon deposition is minimised to ensure a long working life of the stack.

There are opportunities for new catalyst materials both for the MCFC catalyst and the SOFC anode. The ability to run fuel cells directly on hydrocarbons such as natural gas will help to ensure the commercial success of fuel cells in the future.

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