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Peer Review Status: Peer reviewed

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Thursfield A, Murugan A, Franca R, Metcalfe IS. [Chemical looping and oxygen permeable ceramic membranes for hydrogen production-a review](#). *Energy & Environmental Science* 2012, **5**(6), 7421-7459.

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ARTICLE TYPE

Chemical looping and oxygen permeable ceramic membranes for hydrogen production – A review

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Both chemical looping processes and oxygen permeable ceramic membranes require gas-solid surface reaction to occur in order to function; the two approaches have much in common at a fundamental level. Both approaches, through either dynamic operation in the case of looping or membrane operation, allow a degree of process intensification through simultaneous reaction and separation. Here the use of chemical looping and oxygen permeable ceramic membranes for hydrogen production is reviewed. Hydrogen production from water with various reducing gases is covered, as is synthesis gas production from hydrocarbons with various oxidants (this requiring further hydrogen separation from the synthesis gas). The two approaches are compared and contrasted.

Cite this: DOI: 10.1039/c0xx00000x

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1. Introduction

Hydrogen is conventionally produced by steam reforming of hydrocarbons to produce a mixture of carbon monoxide, carbon dioxide, steam and hydrogen. Much of the carbon monoxide is removed by further processing involving high and then low temperature water-gas shift reaction. The resulting stream is then supplied to a pressure swing adsorption (PSA) unit, or other separation process, where hydrogen and carbon dioxide are separated. Recently, in order to produce intensified processes for hydrogen production, there has been considerable interest in the use of chemical looping and high temperature membranes. Both approaches use high temperature gas-solid oxidation and reduction processes for hydrogen production with, depending upon the specific implementation, a degree of separation.

Chemical looping has previously been defined by Moghtaderi¹ as occurring when “a given reaction (e.g., $A + B \rightarrow C + D$) is divided into multiple subreactions with each typically being carried out in a separate reactor”. However the definition need not be restricted to solid intermediates alone as what is critical is the requirement for the products and intermediates to be in different phases for ease of separation. The remarkable, recent increase in interest in chemical looping technology has prompted a number of workers to provide timely monographs, namely, a text by Fan² entitled “Chemical Looping Systems for Fossil Energy Conversions”, a review by Li and Fan focusing on clean coal conversion³, a review by Moghtaderi focusing on the processing aspects of chemical looping technologies¹ and a very recent review from Adanez *et al.* on chemical looping combustion and reforming technologies⁴.

Over the past six years a number of reviews^{5–10} have been published in the area of ceramic oxygen transport membranes (OTMs) applied to a number of hydrocarbon-conversion processes. These articles provide a broad overview of the technology including applications that fall outside of the scope of this review. Liu *et al.*⁶ provide a useful overview of membrane material and transport mechanisms before discussing applications. An earlier review by Yang *et al.*⁷ discussed OTM materials and considered applications such as oxidative dehydrogenation of propane to propene. A briefer contribution by Ushachev *et al.*⁹ outlined problems with synthesis gas production and how OTM technology may be of benefit. In a contribution by Caro, microtubular OTM technology is discussed with applications such as oxidative coupling of methane to C₂ products⁸. The most recent, and lengthier, contributions by Dong *et al.*⁵ and Jian *et al.*¹⁰ provide a more comprehensive presentation of OTM technology including e.g., proton conducting transport membranes and applications outside of the scope of this review.

In contrast to the emphases provided by the above reviews we focus solely on hydrogen production. The chemical looping

section focuses on water-splitting, which yields hydrogen in water vapour (a straightforward separation), with a summary of synthesis gas (carbon monoxide and hydrogen, syngas) production (further shift reaction and separation required) by partial oxidation of methane (POM). An overview of materials employed, their thermodynamic behaviour and their performance under operating conditions is presented. The OTM section of this contribution begins with recent efforts to produce hydrogen from water-splitting. A lengthier section on POM follows, reflecting the larger body of published work in comparison to that for OTM-based water-splitting. We also provide a synopsis of syngas production using other hydrocarbon feeds for completeness. It is not the intention of this review to discuss process economics.

This review will confine itself to chemical looping processes that use solid oxygen carriers; conventionally these carriers tend to be transition metal oxides. There are two main approaches to hydrogen production using oxygen carrier materials (OCMs). The first is reduction of the carrier by a reducing gas followed by oxidation in water. Iron oxide is attractive for this process because the thermodynamics of the FeO/Fe₃O₄ transition allow high hydrogen mole fractions to be achieved. If carbon monoxide is used as the reducing gas the overall process is the water-gas shift (WGS) reaction. Here we name each chemical looping process according to the overall reaction, so the process may be termed as chemical looping water-gas shift (CLWGS). The reduction and oxidation can be defined:

In addition to oxygen removal from a water stream, hydrogen can be produced by oxygen addition to a hydrocarbon stream resulting in reforming and syngas production. If this oxygen is provided by air in the carrier oxidation stage, the overall process will be a partial oxidation of the hydrocarbon feed to syngas (chemical looping partial oxidation, CLPO).

Such processes of course are not intensified in the sense that there is no separation of carbon oxides and hydrogen, and pressure-swing adsorption (PSA) or other separation process must still be employed. However, syngas production is performed in a partial oxidation process (exothermic in nature) as opposed to steam reforming (highly endothermic) potentially avoiding the need for heat supply to the reactor.

15 Our primary concern will be the first type of looping process (e.g., CLWGS) for hydrogen production because of the higher level of intensification. This field has not previously been reviewed in detail with a looping material focus (however both Fan and Moghtaderi have recently addressed this type of process as part of comprehensive chemical looping reviews¹⁻³). For completeness we will also cover chemical looping partial oxidation for syngas production (CLPO) and highlight work of particular note. It should be noted that there is a vast body of literature on the separate processes of metal oxide oxidation and reductionⁱ.

There are striking similarities between chemical looping processes and membrane processes at the reactor level (Figure 1).

ⁱ We make no attempt to review these areas (although we refer to such work when necessary) instead confining this review to work that has dealt with looping cycles, i.e., that has investigated repeated redox cycling, or circulating fluidised beds specifically.

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Figure 1. Schematics representing (a) periodically operated fixed bed chemical looping system (co-current flow), (b) circulating fluidised bed chemical looping system and (c) oxygen permeating membrane system for hydrogen production (co-current flow) for WGS.

In chemical looping the reducing gas reduces the OCM followed by oxidation in e.g. water. The reduction and oxidation processes are separated temporally using a solid phase reference frame. The use of an OCM in powder or pellet form allows gas phase transport within the reactor bed and good access to a large OCM surface area (see Figure 2).

Figure 2. Schematic depicting (a) unconnected particles (b) particles loosely compacted into agglomerates forming structures with a porous network and (c) further densification by sintering to promote grain growth resulting in a gas-tight structure. The black outline around particles represent grain boundaries formed during sintering.

The OCM itself must be able to undergo bulk and not just surface oxidation and reduction if the oxygen storage capacity is to be sufficient for practical applications. Bulk oxidation and reduction of course rely upon solid state transport processes. The analogue to this process in a membrane system is one in which one side of the membrane is exposed to the reducing gas and the other to water. The reduction and oxidation processes are separated spatially and the membrane must transport oxygen (in much the same way as the OCM must be able to undergo bulk and not just surface oxidation and reduction). The membrane must be dense (typically, greater than 95% dense such that there are no interconnected pores resulting in a gas phase path across the membrane), this results in a low surface area. It is interesting to note that if the oxidising and reducing gases are switched in a membrane system the membrane material (itself an OCM) will respond in such a way that hybrid operation involving looping and permeation should be achieved. This has not, to our knowledge, been investigated in the literature but raises an important and poorly appreciated point for membrane studies: it can be difficult to prove that the gas phase changes in a membrane system are due to membrane permeation alone.

Steady state operation and careful use of material balances with information on gas compositions on both sides of the membrane must be used if a full understanding is to be developed.

Solid state transport in these oxides (membranes and OCMs) at the temperatures necessary for e.g. methane activation and water dissociation (greater than *ca* 600°C) involves ionic and electronic mobility. In a membrane, oxygen transport tends to rely upon oxygen anion and electron migration (see Figure 3). Cation migration is often associated with membrane instability and material segregation and would in fact, if exploited as a mechanism of conduction, cause the membrane to move relative to the membrane housing.

Figure 3. Schematic depicting (a) mechanism for oxygen migration at elevated temperature from high oxygen activity (pO_2) to low oxygen activity (pO_2') in a simple $A^{+3}B^{+3}O_3$ perovskite-type crystallite or membrane. $V_O^{\bullet\bullet}$ represents the counter flow of oxygen vacancies and $h^\bullet$ electron holes required for charge neutrality. (b) simultaneously, the constituent cations also migrate, moving from their lattice sites *via* a counter flow of mobile vacancies, $V_A^{\bullet\bullet}$ and $V_B^{\bullet\bullet}$ (both with a net charge of -3), and electron holes to maintain charge neutrality. The diffusion

[Type text]

coefficients for $V_A^{\bullet\bullet}$ and $V_B^{\bullet\bullet}$ may not be equal. The effect is to cause kinetic demixing with depletion and enrichment of the B-site species, B_B^x , at either surface.

In an OCM there is no constraint against exploiting cation mobility as a mechanism of solid state transport and the material may undergo bulk oxidation and reduction through a combination of cation, oxygen anion and electron migration (Figure 3); Fan *et al.* have recently studied such processes in iron oxide and iron oxide sintered with titania^{11, 12}. Furthermore, whereas a membrane must maintain its gas-tight nature to be effective, fragmentation of OCM particles or pellets can be tolerated provided material is not lost from the bed (here fixed bed operation versus circulating fluidised beds with a cyclone exhibit different constraints) to a significant extent and pressure drop is not significantly increased. These constraints mean that a small subset of OCM materials (materials which do not undergo a phase transition and have an anion conductivity that is much greater than their cation conductivity) can also be used for membrane-based processes.

Chemical looping and membrane approaches will be compared and contrasted although some points of difference can be highlighted now. The very different area to mass ratios of an OCM versus a membrane mean that different processes will be rate determining. In a membrane, solid state transport must take place over a longer length scale. The greater activation energies of these bulk transport processes compared to surface processes means that in practice membranes may need slightly higher temperatures of operation. In terms of the purity of hydrogen produced, which is critical for water-splitting processes, a membrane system, if gas tight, should give only hydrogen in water as a product. On the reducing side of the membrane selectivity is not an issue (as the product stream never sees this surface) provided, of course, a process such as carbon deposition does not poison the reducing surface. In the case of chemical looping, carbon formation during reduction will result in carbon being carried over to the water-splitting process and result in carbon monoxide in the product stream. If such side reactions can be avoided in a chemical looping process yielding a hydrogen in water product, it is hard to see how a membrane system can compete because of its unfavourable geometry (longer solid state diffusion lengths and lower specific surface areas). Membranes have the advantage of steady state operation over dynamic packed beds but not, of course, over circulating fluidised beds.

2. Chemical looping processes

2.1. Steam-iron processes (chemical looping water-gas shift over iron oxide)

2.1.1. History (1903-1971)

Many papers refer to Howard Lane, an engineer from Birmingham, UK, as the first inventor of a chemical looping process for producing hydrogen. In 1903, he invented the Lane Hydrogen Producer¹³, this was the first process that alternately

reduced and oxidised iron oxide using the gasified products of coal and water to form pure streams of carbon dioxide and hydrogen. In his article, Lane stated that this process was much more favourable than the other possible processes (e.g., reacting sulfuric acid with zinc/iron or by electrolysis of water)¹⁴ for obtaining pure hydrogen. The sulfuric acid process would give low hydrogen purity, and the electrolysis process would be costly.

In 1911 Messerschmitt¹⁵ patented and gave the name 'steam-iron process' to Howard Lane's invention. A steam-iron process was defined as one which alternately used steam and a reducing gas such as carbon monoxide, syngas or methane to continually oxidise and reduce iron oxide in a chemical looping process. Pure hydrogen product is formed when water is split to oxidise the iron oxide or iron.

Since Messerschmitt's steam-iron process patent in 1911, there was very little research on the process until 1996. A number of patents in addition to a pilot plant study of a fluidised bed reactor for the steam-iron process by Gasior *et al.*¹⁶ in 1961 appear to be the only recorded documents of such research in this time period.

Parsons¹⁷ in 1928 proposed a steam-iron process system employing carbon monoxide reduction and water oxidation whereby the iron oxide material drops downwards under gravity first through the reduction chamber and then through the oxidation chamber, and is carried back to the top of the reactor by a mechanical elevator. By this operation, hydrogen is produced continuously. This is the first design of a steam-iron process where the solid is continuously circulated. Marshall¹⁸ in 1939 proposed a steam-iron system where iron is dropped through a water-splitting reactor by gravity (to produce hydrogen); magnetite at the bottom of the water splitter is transported horizontally (by a conveyor belt) to the reducing furnace. The magnetite is then reduced to iron by a mixture of methane and air to produce carbon dioxide and water. The reduced iron is then recycled back to the top of the water splitter by the use of another conveyor. Reed *et al.*¹⁹ in 1953 devised a three reactor circulating fluidised system utilising iron oxide as the OCM comprising of reduction by a hydrocarbon, air oxidation and water-splitting (in this order). By this method, carbon deposited on the OCM can be removed by the subsequent air oxidation step. The iron oxide would then be free of carbon deposits and can be introduced into the water-splitting reactor to allow the production of pure hydrogen. As a separate claim they state that carbon-laden magnetite (Fe_3O_4) can be reduced to wüstite (FeO) by using a mixture of oxygen and carbon monoxide, thus providing wüstite free of carbon.

Gasior *et al.*¹⁶ attempted to improve contact between the gas and solid phases in a steam-iron process that alternated steam and syngas as the oxidising and reducing agents. This study focused on simple fluidised (not circulating) and free-falling beds. They successfully demonstrated hydrogen production at pilot scale using both natural and synthetic magnetite (magnetite principally with magnesia). Hydrogen mole fractions on a dry basis of 98% were achieved; the balance being carbon monoxide and carbon dioxide. Reaction rates were found to be first order in pressure for both the oxidation and reduction reactions. Most of their

work was performed in the range of 4 to 14 bar, however, they recommended operation at 20 bar for thermodynamic and economic considerations. They found that there were problems above 800°C as this caused agglomeration of the iron particles. At temperatures below 700°C, they found carbon laydown due to the Boudouard reaction. This carbon was found to react with water during the oxidation step to form unwanted oxides of carbon alongside hydrogen. Methane as a potential reducing agent was also investigated.

Watkins in 1962 devised a system that comprised of two separate steam-iron processes²⁰. For the OCM a metal oxide such as iron, nickel or cobalt supported on alumina and/or silica was suggested. In the first system, a reduction reactor (which allowed carbon deposition on the OCM to occur) was used to produce syngas by reducing methane, this was coupled to an air oxidation reactor. The syngas formed by the first steam-iron system, was used as the reducing agent for the second steam-iron system. In the second system, the reduction reactor (which did not allow carbon deposition) was used to produce carbon dioxide and water; the unit was coupled with a water-splitting reactor which could produce hydrogen. Benson in 1969 devised a system that could produce separate streams of methane and hydrogen from carbonaceous fuel, steam and air (using iron oxide as the OCM)²¹. The carbonaceous fuel is initially gasified by a mixture of steam/hydrogen and the solid char formed is used in the steam-iron process whereas the gaseous products (mainly carbon monoxide) are cleaned to remove sulfur, carbon dioxide and hydrogen sulfide. This gas is then used for a separate methane synthesis step. The system additionally involves a step that upgrades carbon dioxide back to syngas by reacting it with char and air. The syngas formed by this step is then used in a second steam-iron cycle to produce further hydrogen from water. Huebler *et al.*²² in 1969 devised a system which, overall, produces separate streams of hydrogen and carbon dioxide/water from water and syngas. In this system there are two reduction reactors, and steam is used to recirculate the iron oxide solid back to the top of the reactors (this is where oxidation of the OCM to provide hydrogen occurs). Syngas is passed through the first reactor, and then through the second, whereas steam flows firstly through the second reactor then the first. This counter-current flow system was adopted in order to maximise hydrogen production (the higher hydrogen partial pressures are achieved in the presence of the most reduced carrier). Johnson in 1971 devised a continuous steam-iron process where carbonaceous solids were used as the reducing agent and steam as the oxidising agent²³. In this system, the carbonaceous solids are finely divided and flow upwards in counter-current flow against the solid iron oxide.

The work prior to 1971 indicates that the steam-iron process is indeed possible in principle. However, there are certain issues that were not adequately addressed. The steam-iron process requires an OCM that can be reduced and oxidised over many continuous redox cycles, and therefore the material must not deactivate during operation. Most of the oxygen carrier materials in these investigations contain iron oxide, but a few papers have also considered alternative materials which use iron oxide doped

with an additional metal, and materials which do not contain iron at all. Additionally, the reducing agent for the process is usually a carbon-containing gas such as carbon monoxide or methane, and therefore carbon deposition can be an issue if pure hydrogen is required.

It should be noted that the steam-iron process can also be used for hydrogen production at a localised site, and can be viewed as a form of hydrogen storage (although hydrogen is not actually stored within the material). This method relies upon reducing iron oxide, transporting the reduced iron oxide to the required location and finally oxidising the reduced iron oxide with water to produce hydrogen. The hydrogen evolution process could potentially be used on board vehicles^{24, 25}. The hydrogen consumption process could potentially be employed at distributed energy generation sites. Renewable energy e.g., tidal or wind is used to electrolyse water to produce hydrogen for the iron oxide reduction²⁶. The advantages of using this method rather than transporting hydrogen include reduction of volumetric storage capacity and safety of handling. Alternatively, the steam-iron process can be used to carry out hydrogen separation from a mixture of hydrogen and other components (which would be the reducing agent)²⁷. By this method, the hydrogen mixture will reduce the oxygen carrier material, and water will be used in the subsequent oxidation step to produce pure hydrogen.

Hydrogen can also be produced by performing cycles of methane cracking and air oxidation²⁸. During methane cracking, the methane is converted into hydrogen, and carbon is deposited onto a metal oxide (such as nickel oxide, which also catalyses the reaction). During this step pure hydrogen is produced:

A subsequent air oxidation step would then be used to remove carbon from the metal oxideⁱⁱ.

2.1.2. Behaviour of iron oxide as an OCM

Oxides of nickel, cobalt, chromium and manganese have been compared thermodynamically for hydrogen production via chemical looping. The reoxidation step in water vapour for many of these oxides results in a low equilibrium hydrogen mole fraction with iron oxide appearing to be the best system; the thermodynamics of this system have been investigated in detail²⁹⁻³¹. It should be noted that iron oxide is also attractive from an economic point of view and also from an environmental and health perspective³².

Iron in the iron oxides used in the steam-iron process usually exists in one of the three oxidation states listed in Table 1. It naturally occurs in the form of iron ore which usually consists of a high percentage of iron oxide with small amounts of impurities such as alumina, silica and quicklime.

Table 1 The oxidation states of iron oxide

	chemical formula	oxidation state(s)
Iron	Fe	0
Iron (II) oxide, wüstite	FeO	+2
Iron (II,III) oxide, magnetite ^a	Fe ₃ O ₄ *	+2,+3
Iron (III) oxide, haematite	Fe ₂ O ₃	+3

^amagnetite exists as a mixture of wüstite and haematite

Wüstite is known to be iron-deficient where the iron/oxygen ratio is actually within the range of 0.83-0.95^{33, 34}. Workers have either chosen a particular iron/oxygen ratio within this range or assumed that the iron oxide is not iron-deficient and this leads to, as Hacker *et al.*³³ explain, a discrepancy in data obtained during thermodynamic analysis.

The Baur-Glaesner phase diagram (as shown in Figure 4)³⁵ indicates that wüstite only exists at temperatures above ~565°C, in agreement with other thermodynamic studies which state that temperatures below 567°C cause instability in wüstite and that only iron or magnetite are thermodynamically stable^{31, 36, 37}. In the presence of a water/hydrogen ratio less than 5×10⁴, haematite is not likely to exist³⁸.

Figure 4. Baur-Glaessner phase diagram depicting phase stability in different virtual pO_2 as a function of temperatureⁱⁱⁱ.

The reactions that can occur between water and iron/iron oxide would occur step-wise:

In early steam-iron processes, carbon monoxide obtained by the gasification of coal was used as the reducing agent.

ⁱⁱ Since this process does not utilise the oxygen capacity of the metal oxide, it will not be discussed further in this review.
[Type text]

ⁱⁱⁱ Reprinted from Catalysis Today, Volume 127, M. F. Bleeker, S. R. A. Kersten and H. J. Veringa, "Pure hydrogen from pyrolysis oil using the steam-iron process", pp 278-290, Copyright (2007), with permission from Elsevier.

It should be noted that thermodynamically, high fuel utilisation is impossible in the presence of Fe_3O_4 ^{31, 39}.

Alternatively, an air reactor can be incorporated into the steam-iron process after the water-splitting step to further oxidise the iron oxide^{40, 41}.

By adding an air reactor to the steam-iron process, additional heat to facilitate process or energy integration is provided. In this way, fuel utilisation in the presence of Fe_2O_3 is improved. The overall cyclic process would be:

In order to obtain good fuel utilisation in the reducer reactor, solid-gas contacting patterns are important to ensure that haemetite comes into contact with the exit gases. Fan *et al.*⁴² have suggested using a counter-current moving bed reducer; Heidebrecht and Sundmacher used a reverse-flow fixed bed⁴³.

2.1.3. Carbon deposition and carbide formation

Gasior found that carbon deposition occurs during the reduction step at temperatures below 700°C when using carbon monoxide as the reducing agent because of the Boudouard reaction⁴⁴.

The reaction of iron oxide with carbon monoxide has been studied by Mondal *et al.*⁴⁵ who produced a plot (Figure 5) presenting the Gibbs free energy of the reactions shown.

Figure 5. Gibbs free energies for iron oxide reactions with carbon monoxide as a function of temperature^{iv}.

^{iv} Reprinted from Fuel Processing Technology, Volume 86, K. Mondal, H. Lorethova, E. Hippo, T. Wiltowski and S. B. [Type text]

As the value of the Gibbs free energy of the Boudouard reaction illustrates, the tendency for the production of solid carbon can be reduced by an increase in temperature. This finding agrees with Gasior's work which proved experimentally that increasing temperature reduces carbon deposition⁴⁴. According to the trends presented in Figure 5, at a lower temperature, the Boudouard reaction should be more thermodynamically favourable. However due to kinetic limitations, the rate of reaction would decrease. Hence, there would be a temperature associated with maximum carbon deposition.

Go *et al.*⁴⁶ investigated carbon deposition during methane pyrolysis and found that carbon formation was likely to occur in the presence of a more reduced iron oxide, in particular iron. Svoboda considered the possible formation of other iron complexes such as iron hydroxide and iron carbonate³¹. Thermodynamic analysis indicated that these species are not likely to be formed in the steam-iron process, especially at higher temperatures (above 527°C). The formation of iron carbide however, was considered possible during carbon monoxide or methane reduction.

A study by Huebler *et al.*²² proved that a small amount of sulfur in the form of hydrogen sulfide (0.1-0.5%) in the reducing feed can actually improve the overall process by inhibiting carbon formation (although this is not discussed further in their study).

2.1.4. Reducing agents

Carbon monoxide is not a primary fuel available for the reduction step and obtaining it in pure form usually requires further processing. This means that the reduction step for steam-iron processes needs to be performed with syngas derived from; coal, biomass gasification or natural gas reforming. Alternatively these fuels (coal, biomass and natural gas) could be fed directly into the reduction stage^v.

Syngas Syngas can be derived from any hydrocarbon source including coal or biomass by a gasification/reforming step. Syngas can then be fed to a looping process as the reducing agent⁴⁷⁻⁴⁹. Both coal and biomass (and indeed natural gas) contain many impurities such as sulfur. Although the deactivation of the OCM is clearly in general a disadvantage, the fact that the material only survives a limited number of redox cycles means that the presence of poisons in the feed stream is not necessarily critical to the process as long as they do not

Lalvani, "Reduction of iron oxide in carbon monoxide atmosphere-reaction controlled kinetics", pp 33-47, Copyright (2004), with permission from Elsevier.

^v Note that if a hydrogen-containing stream is used as the reducing agent then chemical looping hydrogen separation is performed. The kinetics of this process have been studied by E. Lorente, J. A. Peña and J. Herguido, International Journal of Hydrogen Energy, 2008, 33, 615-626 and J. Plou, P. Duran, J. Herguido and J. A. Peña, International Journal of Hydrogen Energy, 2011, In Press, Corrected Proof.

transfer into the gaseous product streams. An investigation by Hacker *et al.*⁵⁰ used simulated syngas from biomass gasification containing hydrogen chloride as the reducing agent to carry out five steam-iron cycles at 800-900°C. They found that the hydrogen chloride transferred from the reducing agent into the oxidation stream, but ends up dissolved in the unreacted water rather than as a contaminant of the product hydrogen stream. A similar test was performed using hydrogen sulfide impurities; no hydrogen sulfide was detected in the hydrogen product stream after five redox cycles. More recently, Müller *et al.* also found no problems with sulfur contamination of the hydrogen product⁴⁸.

Direct Feed Coal A benefit of using coal as the reducing agent is that it is relatively cheap and, compared to natural gas or crude oil, is naturally more abundant⁵¹. Coal can be used directly in the steam-iron process to reduce iron oxide⁵², the advantage of this being the removal of the gasification reactor and a disadvantage being the difficulties from solid-solid mixing⁵³.

The main aim of Yang *et al.*⁵⁴ was to determine the feasibility of introducing coal as a reducing agent into the steam-iron process. Different coal chars were used to directly reduce haemetite (an air oxidation step was employed). High potassium (10% by weight) chars were found to be more attractive as they react at lower temperatures and give higher conversions. However they explain that the cost of adding potassium to char would be too expensive for commercial application.

Direct Feed Biomass A concept study modelling a steam-iron process using direct feed biomass has suggested that the process would be carbon negative (if the pure carbon dioxide produced by the cyclic process is captured and stored)⁵⁵. It is stated that this method of hydrogen production would be competitive compared with conventional methods with a carbon credit of \$20 per tonne. Alternatively, biomass can be converted into pyrolysis oil by rapidly heating the solid biomass in the absence of air with the pyrolysis oil then being fed to a looping process^{35, 56}.

Natural gas Methane can be either fully oxidised or partially oxidised by iron oxide to produce either carbon dioxide with water or carbon monoxide with hydrogen (the WGS reaction means that product streams including carbon monoxide, carbon dioxide, hydrogen and water are also possible). Selectivity can be controlled in a circulating fluidised bed reactor by changing the iron oxide to methane ratio⁵⁷. A higher ratio of iron oxide to methane would induce full oxidation, whereas a lower iron oxide to methane ratio would more likely result in partial oxidation of methane.

Go *et al.*⁴¹ recognised that there existed a conceptual design for the steam-iron process using methane as the reducing agent. They investigated the feasibility of such a process and determined suitable conditions for operation⁴⁶. Experiments were carried out using thermogravimetric analysis (TGA) to follow redox cycles. They state that a reduction temperature above 800°C and oxidation at 900°C should be used to cycle the OCM between wüstite and magnetite. The process was selective for total oxidation of the methane feed at magnetite to wüstite conversions

of less than 50% and syngas for conversions greater than 50%.

Alternative reducing agents Hydrocarbon fuels other than coal, biomass and natural gas have been tested as potential reducing feeds in the steam-iron process, where the hydrocarbon is either initially gasified into syngas or fed directly as the reducing agent.

Residual oil (a side product from petroleum refineries) was used as the reducing agent in a steam-iron process where coke was intentionally deposited on magnetite by thermal cracking⁵⁸. The coke-deposited magnetite was transferred to an air oxidation chamber where air was used to convert coke to carbon monoxide, which subsequently reduced the magnetite to wüstite. The wüstite was then transferred to the steam oxidation reactor to perform water-splitting. It was found that hydrogen production declined as the process continued as a result of structural changes and accumulation of wüstite.

2.1.5. Improving stability and reactivity of iron-containing OCMs

Cyclability of iron oxide is a major issue during the steam-iron process as poor cyclability leads to reduced hydrogen production to the point at which the iron oxide needs to be replaced. In terms of mechanical strength, fresh pellets of iron oxide appear to have sufficient strength to withstand the conditions in a steam iron process. Hacker tested the compressive strength of different iron oxide phases in the form of commercially available porous iron ore pellets³³. However aged pellets may have different properties and reduced mechanical strength; no study seems to have investigated this issue in depth.

A recent paper by Bohn *et al.* investigated the cyclability of iron oxide³⁸. The idea was to see if reduction to iron resulted in excessive loss of surface area and a decrease in OCM performance. They carried out 10 cycles of reduction and oxidation, with water, at 600, 750 and 900°C. In one set of experimental runs the iron oxide was reduced using carbon monoxide as the reducing agent (this was expected to produce iron). In another set the iron oxide was reduced in an equimolar mixture of carbon monoxide and carbon dioxide (this was expected to produce wüstite rather than iron as suggested by the thermodynamics represented in Figure 4). In the case of wüstite formation the reactions would be:

Note that the oxidation of wüstite to magnetite produces one quarter of the hydrogen that the oxidation of iron to magnetite would produce.

The results indicated that each reduction in carbon monoxide/carbon dioxide produced a small but constant amount of hydrogen (with less than 25 ppm of carbon monoxide) over the ten cycles for all three temperatures. However, for the runs involving reduction in carbon monoxide, initially higher amounts of hydrogen were produced but this dropped to very low levels as the cycles progressed (although hydrogen purity remained good).

The results confirmed that reduction to iron instead of wüstite does indeed allow the production of larger amounts of hydrogen initially but at the cost of lower production as the cycles progress. In a redox cycle where stability of the material is important, it may be preferred to produce slightly lower amounts of hydrogen but at a constant level over a larger number of cycles. Post-operation material characterisation, which may have determined the cause for deterioration of the OCM, was not performed.

The experiment was then repeated with fresh material but this time including an additional air oxidation step for every cycle. This step would convert magnetite to haematite:

Using an air oxidation step showed marginal difference in hydrogen production levels, but it was noted that benefits would be heat production and removal of carbon impurities from the OCM.

Iron oxide composites An alternative approach to improving stability, rather than introducing carbon dioxide into the reducing feed, is to support the iron oxide on an inert material^{59, 60}. The concept is to construct a material that inhibits surface area loss even when the carrier is reduced to iron (the reduction to iron allowing greater hydrogen production than reduction to wüstite).

Bohn *et al.*⁵⁹ modified iron oxide with salts of aluminium, chromium, magnesium and silicon by a co-precipitation method. Steam-iron cycles were carried out using carbon monoxide or hydrogen as the reducing agent at 850°C, both with and without air addition. Out of the different salts tested, the addition of aluminium gave the greatest improvement in cyclability compared to unsupported iron oxide.

Kierzkowska *et al.*⁶⁰ compared four samples of composite iron oxide and alumina synthesised by the sol-gel method with different iron oxide-to-alumina mass ratios. These four ratios were 60:40, 80:20, 90:10 and 100:0. Forty redox cycles using carbon monoxide as the reducing agent and water as the oxidising agent were performed. Oxygen carriers with a loading of 10-20 wt% of alumina saw a small drop in activity and hydrogen conversion, whereas the sample with a loading of 40 wt% alumina gave very little drop in performance over 40 cycles but the initial performance was lower. They explain that during the initial cycles, the iron oxide reacts with alumina to form the spinel (FeO.Al₂O₃) which stabilises the OCM, leading to steady hydrogen production. For this reason, they selected 60% haematite supported on alumina as the best candidate oxygen carrier material for the steam-iron process over 40 cycles.

Naturally occurring iron oxide materials Sponge iron, also known as direct reduced iron, has been employed as an OCM for the steam-iron process. It is described as an iron-containing metal oxide that is formed by reducing iron ore with either natural gas or coal⁶¹. Some researchers have attempted to simulate direct reduced iron by reacting haematite with carbon to form iron oxide-carbon composite pellets⁶². Sponge iron produced by the first method usually contains other minerals such

as silica, quicklime and alumina⁶³ whereas the second method would form material containing only carbon and iron oxide.

Increasing silica and alumina content have proven to improve stability, which could explain why in a comparison between Sek and Malmberget pellets (by performing sponge iron cycles using both carbon monoxide and hydrogen as the reducing agent), the former shows higher stability during redox cycling tests⁶³. The composition of Sek and Malmberget pellets are shown in Table 2.

Table 2 Compositions of Sek and Malmberget Pellets (as a percentage of total weight)

	Sek	Malmberget
Fe	57.83	66.70
SiO ₂	7.96	1.16
Mn	0.03	0.06
CaO	3.91	1.21
O	1.04	0.81
Al ₂ O ₃	0.39	0.33
P	0.01	0.033
S	0.024	0.001
Na	0.075	0.045
Ti	0.025	0.10
K	0.094	0.03
Zn	0.025	0.0038
Pb	0.001	0.0002

Additional results (not provided in the paper) apparently showed that using carbon monoxide as the reducing agent allowed the production of hydrogen with trace amounts of carbon monoxide and carbon dioxide in the hydrogen product stream. However, the term ‘trace’ is vague and the amount is not quantified.

Kindermann *et al.*⁶⁴ and Thaler *et al.*⁶⁵ investigated how haematite content and pellet composition in general affects performance in sponge-iron processes using hydrogen and carbon monoxide as reducing agents. Further tests using different reducing agents and operating temperatures show that changing experimental conditions can affect which compositions of the sponge iron material would give the best performance. Hacker *et al.* suggests that the acidity or alkalinity of the sponge iron pellet is a determining factor⁶⁶. Alkalinity was defined as:

$$\text{Alkalinity} = \frac{\text{wt\% CaO} + \text{wt\% MgO}}{\text{wt\% SiO}_2 + \text{wt\% Al}_2\text{O}_3} \quad (24)$$

Their results indicated that a higher alkalinity above 600°C gave higher reaction rates, whereas below this temperature a higher alkalinity gave lower rates.

Alternative iron-containing phases Perovskite materials (general formula ABO₃) have previously been used in the form of dense gas-tight membranes for water-splitting (this is further discussed in Section 3). In an investigation by Murugan *et al.*⁶⁷ perovskites were tested as OCMs for a chemical looping WGS process. In an initial test five temperature programmed reduction (using carbon monoxide) and oxidation (using water) cycles up to 1000°C were

performed using the perovskites $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ and $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_{3-\delta}$. The same procedure was applied to 20 wt% $\text{NiO}/\text{Al}_2\text{O}_3$ and 60 wt% $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ for comparison. The results indicated that the two iron-containing perovskites could provide both high material stability and high purity hydrogen over the five cycles; this was not achieved using the 20 wt% $\text{NiO}/\text{Al}_2\text{O}_3$ and 60 wt% $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ OCMs. Chemical looping WGS using $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_{3-\delta}$ as an OCM produced hydrogen (with carbon monoxide content less than 100 ppm, although this was not accurately quantified due to possible nitrogen ingress and analysis by mass spectrometer – nitrogen and carbon monoxide both having $m/z=28$) over more than 120 redox cycles. Post operation characterisation by XRD and SEM indicated that after 150 redox cycles $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_{3-\delta}$ showed no change in crystal phase purity. The perovskite phases $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_{3-\delta}$, $\text{La}_{0.7}\text{Sr}_{0.3}\text{Cr}_{0.1}\text{Fe}_{0.9}\text{O}_{3-\delta}$ and $\text{La}_{0.7}\text{Sr}_{0.3}\text{Cr}_{0.05}\text{Fe}_{0.95}\text{O}_{3-\delta}$ were investigated by Nalbandian *et al.*⁶⁸. Nickel oxide addition to the perovskites was also investigated. Cycling was limited and although hydrogen yields were reported to be high the performance was not compared to a reference material.

High temperature (800-900°C, with in this case the intention of achieving these temperatures by direct irradiation by visible light) steam-iron processes with methane as the reducing agent were considered by Komada *et al.*⁶⁹. Mixed metal oxides of iron with the general formula $\text{M}_{0.39}\text{Fe}_{2.61}\text{O}_4$, where M represents either nickel, cobalt or zinc (prepared by coprecipitation) and the nickel system supported on zirconia were investigated. $\text{Ni}_{0.39}\text{Fe}_{2.61}\text{O}_4$ produced a much higher yield of syngas compared to the same composition with cobalt or zinc. $\text{Ni}_{0.39}\text{Fe}_{2.61}\text{O}_4/\text{ZrO}_2$ showed no evidence of activity loss over five cycles, however carbon deposition was noted.

Peña *et al.*²⁷ compared the performance of NiFe_2O_4 and CuFe_2O_4 to iron oxide. This investigation focused on the reduction step using both methane and hydrogen. In hydrogen, CuFe_2O_4 allowed the reduction to start at a lower temperature compared to that for NiFe_2O_4 which in turn was an improvement over iron oxide. Due to its performance Kang *et al.*⁷⁰ used CuFe_2O_4 to perform cycles of methane reduction (at 900°C) and water-splitting (at 800°C). The results indicated faster reduction kinetics, lower carbon deposition and higher selectivity for partial oxidation for this material compared to iron oxide. Further tests were carried out using ZrO_2 and CeO_2 as support materials for CuFe_2O_4 ; the results showed that both supports improved methane conversion and material stability⁷¹. Although oxidation by water was performed, these studies focused on methane-to-syngas conversion during the reduction steps. Hydrogen production during the water-splitting step appears not to have been quantified. To determine whether these materials could be used in a chemical looping process to produce pure hydrogen, the oxidation step would require further investigation.

Addition of stabilisers and promoters Otsuka *et al.*²⁴ added 3 mol. % of different metals to iron oxide by coprecipitation with the intention of accelerating rates of reaction to allow redox cycling at low temperatures. Reduction was performed at 330°C with hydrogen as the reducing agent (oxidation was performed

with water at 380°C). Of the metals tested, addition of aluminium, chromium, zirconium, gallium and vanadium gave the best improvement in rates of hydrogen formation during the water-splitting step. A following study (comparing 26 different metal additives) indicated that the noble metals ruthenium, rhodium, palladium, silver and iridium could enhance water-splitting (with rhodium giving the largest improvement)²⁵. Takenaka *et al.* tested molybdenum and rhodium additives by comparing iron oxide samples containing only molybdenum, only rhodium and a mixture of both⁷². SEM showed that the addition of molybdenum prevented sintering which was particularly pronounced in the presence of rhodium; rhodium itself increased reactivity. Urasaki *et al.*⁷³ tested palladium and zirconium additives (introduced by impregnation at low weight (< 1 wt%) loadings) for iron oxide modification. Both gave an improvement in the rate of oxidation by water, while only palladium accelerated the reduction by hydrogen. A low operating temperature of 450°C was used.

An alternative strategy is to try to stabilise the OCM capacity through addition of a promoter. A study was performed to assess the improvement in material stability of adding small amounts (3 mol. %) of ‘metal’ to iron oxide. Chemical looping cycles involving reduction by hydrogen and oxidation by water at 330°C were performed on iron oxide samples each containing one of 26 different metal additives. The results indicated that aluminium, molybdenum and cerium additives gave the largest improvement in stability and increased hydrogen production, although it was stated that scandium, titanium, vanadium, chromium, yttrium and zirconium also improved stability compared to pure iron oxide²⁵. Lorente *et al.*⁷⁴ studied the addition of aluminium, chromium and cerium (by their nitrates) in the preparation step. The additives improved stability but did not improve activity. Galvita *et al.*⁷⁵⁻⁷⁷ performed stability studies using a ceria-zirconia-modified iron oxide. Ceria improved reducibility of the OCM and zirconia improved the overall material stability by retarding iron formation⁷⁸. In a separate study, chromia was added to the ceria-zirconia-modified iron oxide resulting in a reduced rate of material sintering. This provided steady hydrogen production over 100 cycles using syngas as the reducing agent and steam as the oxidising agent⁷⁹. The carbon monoxide content of the hydrogen product was less than 10 ppm. Impregnating 2 wt% molybdenum to form 2% molybdenum-modified 80% Fe_2O_3 -20% $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ resulted in steady hydrogen production over 90 redox cycles⁸⁰. It was suggested that molybdenum slowed down sintering of iron-containing species. Yamaguchi *et al.*⁸¹ also studied ceria-zirconia-modified iron oxide; stability was improved as similarly demonstrated by Galvita *et al.*⁷⁵.

2.1.6. Alternatives to iron-containing OCMs

Miyamoto *et al.*⁸² tested germanium oxide supported on alumina as a possible OCM and directly compared it to iron oxide (hydrogen was used as the reducing agent). The results showed that germanium oxide provided higher yields of hydrogen during water-splitting compared to unsupported iron oxide. Germanium oxide dispersion over the alumina support was used to explain the increase in hydrogen yield compared to using no support. Nickel

as an additive (introduced by impregnation at unspecified loading) at 700°C increased the yield of hydrogen during water-splitting.

Kodama *et al.*⁸³ used various metal oxides for reduction by methane and oxidation by water (CLSMR). Tungsten oxide exhibited a higher reduction rate than iron oxide. However, there appears to be no comparison between the different materials for the water-splitting step. In a further test, tungsten oxide supported on silica, alumina and zirconia was used to perform one redox cycle. The zirconia-supported tungsten oxide gave the most improvement in reactivity for both the reduction and oxidation steps. It was concluded that tungsten oxide could perform redox cycling to produce syngas and hydrogen from reduction by methane and oxidation by water at 1000°C without carbide formation. However, the authors do not mention whether oxides of carbon were observed in the hydrogen product stream. Sim *et al.*⁸⁴ also looked at reduction by methane and oxidation by water using tungsten oxide doped with ceria and zirconia; XRD indicated that WO₃ was primarily present in a monoclinic phase. Ceria and zirconia addition were found to be critical if carbon oxide production was to be avoided in the hydrogen production phase.

Otsuka *et al.*⁸⁵ performed redox cycles using cerium oxide as the OCM (using hydrogen or carbon monoxide as the reducing agent and water as the oxidising agent); iron oxide was not used as a comparison material. Performing reduction by hydrogen at 600°C and water oxidation at 300°C showed a decrease in surface area of the material over seven cycles, although this did not seem to reduce rates of reaction. The addition of palladium, platinum and nickel oxide gave a very small increase in rate of reduction but significantly improved water oxidation rate.

2.1.7. Inclusion of an air oxidation step

The steam-iron process was traditionally implemented in two fluidised beds, one being the fuel reducer and the other being the water oxidiser. Fan *et al.*⁴⁰ introduced the three-reactor concept; reducer, water oxidiser and air oxidiser. Iron oxide was selected as the OCM; magnetite oxidation in air occurred in the solids pneumatic conveying system. In parallel, apparently independently, Chiesa *et al.*⁴¹ suggested a similar process. This three-reactor concept has the advantage that it can be operated autothermally with good fuel utilisation. Kang *et al.*⁸⁶ studied this system operating on a methane feed from a thermodynamic point of view in order to select a suitable OCM. They concluded that iron, ceria and tungsten oxides were worthy of consideration. Furthermore they recommended that reducing gases contact a high oxidation state OCM to obtain good fuel utilisation. Xiang *et al.*⁸⁷ developed an ASPEN model with syngas from coal-gasification as the input and iron oxide as the OCM. Similarly to Kang *et al.* they recommended the reducing gases be contacted with a high oxidation state OCM, in this case in a dual-bed reducing reactor. The same group looked at the experimental implementation of the three-reactor concept^{88,89} and concluded that iron supported on alumina was a suitable OCM, showing no deterioration in performance on cycling (note however that only

ten cycles were used). Kidambi *et al.*⁹⁰ studied the iron oxide/alumina system as an OCM for this process. The presence of hercynite (Fe₂AlO₄) after reduction of the carrier in carbon monoxide and carbon dioxide was confirmed by XRD. When an air oxidation step was used in the cycling protocol hydrogen production remained higher than in the absence of oxidation. Optical imaging of the particles showed the presence of large macropores when oxidation was used in contrast to the absence of such pores when oxidation was not employed. This was explained, with reference to the Fe-Al-O phase diagram, by the oxidation step causing decomposition of the hercynite and formation of haemetite and alumina. The phase change modified the particle microstructure.

Li and Fan have also explored direct coal feed into a three-reactor system for hydrogen production³.

2.1.8. Fixed bed reactor systems

Conventionally chemical looping reactions are implemented in fluidised bed reactors with solid transport between the different reactors by, e.g., pneumatic conveying. The same chemistry can be implemented in a non-steady system or dynamically operated fixed bed reactor. In this implementation, rather than conveying the solid from one reactor to another, the solid is in a fixed position and the gas composition is varied. This has the advantage of simplicity in terms of the solids handling and reactor design, but the disadvantage of transient outlet gas compositions that would in a practical system require beds operating in parallel to ensure appropriate quality and continuity of product supply. Heidebrecht and Sundmacher developed a model of such a dynamic reactor in order to explore the thermodynamic limitations of the system for CLWGS⁴³. Iron oxide was used as the oxygen carrier (note that the authors confused the meanings of haematite and magnetite). The reactor was operated in reverse flow mode^{vi}, i.e., the oxidising and reducing gases were fed to opposite ends of the reactor. Chemical equilibrium was assumed, as the reactor was operated isothermally, and wave analysis performed. The behaviour of the reactor was found to be dominated by the movement of sharp reaction fronts (the 'sharp' nature of the fronts being the result of the infinitely fast kinetics implicitly assumed when adopting an equilibrium approach). The performance of the system is complex to analyse but a regime in which the phase boundaries between iron and wüstite, and wüstite and magnetite are at opposite ends of the bed gave a good balance between fuel utilisation and hydrogen product mole fraction.

2.2. Chemical looping partial oxidation

Partial oxidation of methane to syngas can be performed in a chemical looping process using methane as the reducing agent

^{vi} Previously it has been argued that there are analogues for looping processes, or periodically operated processes, and membrane processes. Reverse flow here can be considered to be an analogue to counter-current flow in a membrane system.

and air as the oxidising agent:

In the area of chemical looping this process is often known as chemical looping reforming. The individual steps, with e.g., nickel oxide as the OCM, are:

This process, which was first patented by Gilliland in 1954⁹¹, is attractive in that syngas can be produced from e.g., a methane feed through an exothermic process as opposed to conventional steam methane reforming which is highly endothermic. However it should be noted that the process may need to be pressurised to run economically⁹². The primary focus of this section of the review is the chemical looping production of pure hydrogen. Therefore, since chemical looping reforming can only provide hydrogen as a component in syngas, in the interests of brevity, a table summarising the key features of the relevant work has been included (Table 3)^{57, 93-115}. Note that this area has also recently been reviewed by Adanez *et al.*⁴. Most of the investigations listed in Table 3 have utilised methane as the reducing agent; the addition of water to the reducing feed was used in some cases to enhance methane reforming. It should be noted, however, that e.g., in the case of a Ni/NiO carrier, reduction to nickel will result in steam methane reforming occurring in the absence of further solid phase reduction. This will, if allowed to proceed, result in an overall endothermic process. Oxides of nickel, cobalt, iron, manganese and copper, found to be suitable for chemical looping combustion processes, were initially tested as OCMs for chemical looping partial oxidation. Unlike chemical looping water-splitting processes (CLWGS and CLSMR), chemical looping partial oxidation does not generate hydrogen by splitting water over the reduced OCM. This suggests that iron oxide is not necessarily the most suitable OCM for such processes. From the literature, it is generally found that nickel-based OCMs are most suitable in terms of reaction rate and hydrogen selectivity. Other OCMs such as those from the perovskite family $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ and the fluorite family Ce-Fe-O were found to give high selectivity towards syngas with good material stability during repeated redox cycling (more than 10 redox cycles have been performed with these OCMs)^{107, 112}.

Rydén and Lyngfelt have investigated the use of chemical looping combustion to provide the energy for steam methane reforming¹¹⁶. Better heat transfer between the OCM and the reformer tubes can potentially lead to higher hydrogen yields; this indirect use of chemical looping in hydrogen production is not discussed further in this review.

2.3. Combined chemical looping with calcium looping processes for hydrogen production

Chemical looping partial oxidation processes can be coupled with carbon dioxide removal by sorption so that both oxygen (by

chemical looping) and carbon dioxide can be exchanged between separate streams using solid carrier materials. The material used for carbon dioxide removal is usually calcium oxide. Dupont *et al.*¹¹⁷ studied various carbon dioxide sorption materials and selected dolomite (a calcium and magnesium-containing carbonate) for further study^{vii}. In sorption-enhanced chemical looping partial oxidation for hydrogen production (also called unmixed steam reforming of methane, an air reactor is used to typically oxidise nickel and regenerate calcia as shown in Equations 28 and 29:

In this oxidation step any carbon present will also be removed¹¹⁷. The oxidised nickel and regenerated calcia can then be transferred to the fuel reactor where methane is introduced. Additional water added to the fuel reactor allows the WGS reaction to occur converting carbon monoxide and water to carbon dioxide and additional hydrogen:

However, Dupont *et al.*¹¹⁷ noted that water addition was not necessary as carbon formation was short lived and water is generated on reduction of nickel oxide. The calcia present in the fuel reactor captures the carbon dioxide to form calcium carbonate:

This ideally leaves only hydrogen as the gaseous product. Typical hydrogen mole fractions achieved are around 80-90% on a dry basis^{117, 118} (the balance being methane, carbon monoxide and primarily carbon dioxide). A clear advantage of this approach is the system can be operated autothermally¹¹⁸. The endothermic calcination occurs at the same time as the exothermic nickel oxidation; the endothermic nickel reduction and methane reforming occur at the same time as the exothermic carbonation. Furthermore, sulfur present in the fuel feed does not appear in the hydrogen product but rather leaves as sulfur dioxide during regeneration of nickel and calcia¹¹⁸. Da Silva and Müller¹¹⁹ have used thermodynamics to validate the approach of Dupont *et al.* using some of their experimental data¹²⁰.

Abanades *et al.*^{121, 122} have studied a variant of this process with the intention of releasing the carbon dioxide as a concentrated stream rather than dilute in nitrogen. They investigated a process using design tools in which copper/copper oxide was used as the OCM and calcia as the carbon dioxide sorbent. The idea was to regenerate copper oxide with air in the absence of calcination.

^{vii} An extensive review of sorption-enhanced hydrogen production has recently been written by D. P. Harrison, Industrial & Engineering Chemistry Research, 2008, 47, 6486-6501 (note that this review covers catalytic reforming combined with carbon dioxide sorption and not chemical looping reforming with carbon dioxide sorption).

This required an operating pressure for this step of 20-30 atm (or slightly higher in their later work¹²²) and a temperature of 850°C. Regeneration of the calcia then takes places at the same time as copper oxide reduction in the presence of a fuel, leading to the
5 production of carbon dioxide and water (this step requires a pressure of 1 atm or lower^{viii}). The hydrogen production step involves a fuel and steam feed with conversion (reforming, water-gas shift and carbonation) taking place over the copper (as a catalyst); calcium carbonate is generated.

10 Rydén *et al.*¹²³ proposed a three fluidised bed process to overcome the problem of carbon dioxide production at low mole fraction. They suggested feeding nickel oxide and calcia to the ‘reforming’ reactor in much the same way as put forward by Dupont. The produced nickel and calcium carbonate are fed to
15 the calciner where calcination takes place in the absence of an air feed. The solids flow from the calciner is split into two and some is fed to the air reactor where nickel oxide is produced. This nickel oxide is returned to the calciner. The rest of the solids flow from the calciner is returned to the ‘reforming’ reactor. In
20 this way carbon dioxide produced on calcination is separated from the oxygen-depleted air produced on oxidation of the OCM.

Other hydrocarbons can be used instead of methane as the reducing feed for sorption-enhanced hydrogen production. Dupont *et al.*¹²⁰ used sunflower oil as the reducing feed (at
25 600°C) and dolomite as the carbon dioxide sorbent to obtain a hydrogen purity of 93%. They stated that more work is required for this process in terms of achieving autothermal operation, avoiding coke deposition and testing for effects of impurities in the hydrocarbon source. They also suggest that other
30 hydrocarbons such as biomass pyrolysis oils and waste oils could be investigated as potential reducing agents. Pimenidou *et al.*¹²⁴ used waste vegetable oil as the reducing agent, nickel supported on alumina as the OCM and dolomite as the carbon dioxide sorbent to perform six redox cycles at 600°C. There were no
35 “obvious” signs of a drop in conversion or hydrogen purity (remaining greater than 95%).

^{viii} Note that the OCM is actually being used here for complete combustion of the fuel and strictly this work could be considered out of the scope of this review.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Table 3 Summary of chemical looping reforming investigations (partial oxidation to syngas)

OCM	Support	Sample weight	Gas composition(s)		Temperature range	Reactor type ^a	Number of cycles/pulses	Cycle time	Post op ^a analysis ^b	ref
			Oxidant	Reductant						
			g	mole fraction	degC			seconds/minutes		
18 wt% NiO 21 wt% NiO	(i) α -Al ₂ O ₃ (ii) γ -Al ₂ O ₃	(i),(ii) 1500	(i),(ii) air 0.21	(i),(ii) CH ₄ 0.5 with H ₂ O 0-0.5	(i),(ii) 800-900	CFB (and TGA)	X	(i),(ii) X	(i),(ii) density tests, crushing strength, SEM, EDS, XRD, BET, TGA	57
(i) MnO (ii) Mn ₂ O ₃ (iii) Mn ₃ O ₄ (1 m ² g ⁻¹) (iv) Mn ₃ O ₄ (8 m ² g ⁻¹)	(i)-(iv) None	(i)-(iv) 0.08	(i)-(iv) O ₂ 0.05	(i)-(iv) H ₂ X (i)-(iv) CH ₄ 0.01	(i)-(iv) 350-850 & 400-900	B	(i)-(iii) X (iv) 4	X	TEM	93
(i) 20 wt% CeO ₂ (ii) 0.5 wt% Pt/20 wt% CeO ₂ (iii) 0.5 wt% Rh/20 wt% CeO ₂	(i)-(iii) Al ₂ O ₃	(i)-(iii) 0.5	(i)-(iii) O ₂ 1.0 or CO ₂ 1.0	a-(i)-(iii) H ₂ 0.07 b-(i)-(iii) CH ₄ 1.0	a-(i)-(iii) 25-700 b-(i)-(iii) 700	B	a-(i)-(iii) X b-(i)-(iii) 28 pulses	a-(i)-(iii) X b-(i)-(iii) X	a-(i)-(iii) X b-(i)-(iii) XRD	94
La _{0.8} Sr _{0.2} Co _{0.5} Fe _{0.5} O _{3-δ}	None	1.67	air 0.21	CH ₄ X	750-950	B	1 per temperature step	X	X	95
(i) 35 wt% NiO (ii) 41 wt% CuO (iii) 39 wt% Fe ₂ O ₃ (iv) 47 wt% Mn ₃ O ₄	(i)-(iv) SiO ₂	(i)-(iv) 10 & (i)-(iv) 15	(i)-(iv) O ₂ 0.05	(i)-(iv) CH ₄ 0.5 & H ₂ O (i),(iii),(iv) 0.5	(i),(iii),(iv) 700-950 (ii) 700-900	FB	(i)-(iv) 1-5	(i)-(iv) ~120 s	(i)-(iv) SEM, XRD	96
(i) 36.5 & 34.5 wt% NiO (ii) 31.8 & 39.4 wt% Fe ₂ O ₃ (iii) 46.0 & 47.0 wt% Mn ₂ O ₃ (iv) 43.0 & 41.3 wt% CuO	(i)-(iv) SiO ₂ & MgAl ₂ O ₄	0.02	O ₂ 0.05	CH ₄ 0.1 & H ₂ O 0.1 & CO ₂ 0.05	(i) 800-1000 (ii),(iii) 800-950 (iv) 800	TGA	> 4	360-1350 s	SEM	97
60 wt% NiO	40 wt% MgAl ₂ O ₄	350	air 0.21	(i) C _{1.154} H _{4.255} O _{0.024} N _{0.007} 1.0 (ii) C _{1.154} H _{4.255} O _{0.024} N _{0.007} 0.75 with 0.25 H ₂ O	(i) 862-925 (ii) 824-923	CFB	X	(i) 140-260 mins (ii) 80-240 mins	X	98
(i) 11 wt% NiO (ii) 16 wt% NiO (iii) 21 wt% NiO (iv) 26 wt% NiO (v) 28 wt% NiO	(i),(iv) α -Al ₂ O ₃ (ii) θ -Al ₂ O ₃ (iii),(v) γ -Al ₂ O ₃	(i)-(v) 300-400	(i)-(v): a-air 0.21 b-O ₂ 0.1-0.15	a-(i)-(v): CH ₄ 0.15 with H ₂ O 0.2 & H ₂ 0.10 b-(i)-(v): CH ₄ 0.25 with H ₂ O 0.075-0.175	(i)-(v): a-400-1000 b-800-950	(i)-(v): a-TGA b-BFB	≥10	400-1000 s	X	99
(i) 40 wt% NiO (ii) 60 wt% NiO	(i) NiAl ₂ O ₄ (ii) MgAl ₂ O ₄	15	O ₂ 0.05	CH ₄ 0.5 with H ₂ O 0.5	800-950	a-(i),(ii) B b-(i),(ii) B	b-(i),(ii) 6-20	a-(i),(ii) 2000-3000 s b-(i),(ii) 2500 s	X	100

(i) 18 wt% NiO (ii) 21 wt% NiO (iii) 20 wt% NiO	(i) α -Al ₂ O ₃ (ii) γ -Al ₂ O ₃ (iii) MgAl ₂ O ₄	(i) 180-250 (ii) 170 (iii) 250	(i)-(iii) air 0.21	a-(i)-(iii) C _{1.14} H _{4.25} O _{0.01} N _{0.005} 1.0 b-(i)-(iii) C _{1.14} H _{4.25} O _{0.01} N _{0.005} 0.7 & H ₂ O 0.3 c-(i)-(iii) C _{1.14} H _{4.25} O _{0.01} N _{0.005} 0.7 & CO ₂ 0.3	a-(i),(ii) X (iii) 950 b-(i) 800-950 (ii) 800-951 (iii) 800-949 c-(i) 951 (ii) 843- 950 (iii) 869-950	CFB	X	a-(i),(ii) X (iii) 130,133,135 mins b-(i) 75-148 (ii) 72- 248 mins (iii) 120- 238 c-(i) 85-115 mins (ii) 96 mins (iii) 60- 120 mins	SEM,XRD	101
(i) La _{0.5} Sr _{0.5} Co _{0.5} Fe _{0.5} O _{3-δ} (ii) La _{1-x} Sr _x FeO _{3-δ} (x=0,0.2,0.5) (iii) 60 wt% NiO (iv) 40 wt% Fe ₂ O ₃ (v) 40 wt% Mn ₂ O ₄ (vi) = 99 wt% (iv) + 1 wt% (iii) (vii) = 90 wt% (iv) + 10 wt% (iii) (viii) = 97 wt% (v) + 3 wt% (iii) (ix) = 90 wt% (v) + 10 wt% (iii)	(i),(ii) none (iii),(iv) MgAl ₂ O ₄ (v) Mg-ZrO ₂ (vi)-(ix) as for (iii),(iv) & (v)	1	air 0.21	(i),(ii) CH ₄ 0.15-0.25 (iii),(ix) CH ₄ 0.5	900	B	(i),(ii) 1-10 (iii)-(ix) 1-5	>11.5 mins	XRD?	102
NiO	(i) NiAl ₂ O ₄ (ii) MgAl ₂ O ₄	(i),(ii) X	(i),(ii) air 0.21	(i),(ii) CH ₄ ~0.98	(i),(ii) 750-900	CFB	X	(i),(ii) X	(i),(ii) X	103
NiO	(i) NiAl ₂ O ₃ (ii) α -Al ₂ O ₃ with MgO	(i),(ii) X	(i),(ii) air 0.21	(i),(ii) CH ₄ ~0.98	(i),(ii) 800-900	CFB	X	(i),(ii) X	(i),(ii) X	104
21 wt% NiO	γ -Al ₂ O ₃ with NiAl ₂ O ₄	~1500	air 0.21	CH ₄ 0-0.5 with H ₂ O 0- 0.25	800-900	FB (and TGA)	X	X	SEM,EDS,XRD BET,TGA	105
(i) CeO ₂ (ii) Ce-Fe-O (5:5) (iii) Ce-Cu-O (5:5) (iv) Ce-Mn-O (5:5) (v) Ce-Fe-O (7:3)	(i)-(v) none	(i)-(v) 1.8	(i)-(v) air 0.21	(i)-(v) CH ₄ 1.0	(i)-(v) 600-900	B (and TGA)	(i)-(v) 20	(i)-(v) ~2000 s	(i)-(iv) X (v) SEM,EDS,XRD	106
(i) La _{0.8} Sr _{0.2} Fe _{0.8} Co _{0.2} O _{3-δ} (ii) 0.5 wt% Rh/La _{0.8} Sr _{0.2} Fe _{0.8} Co _{0.2} O _{3-δ} (iii) La _{0.75} Sr _{0.25} Fe _{0.6} Co _{0.15} Al _{0.25} O _{3-δ} (iv) 0.1,0.5,1.0 wt% Rh/ La _{0.75} Sr _{0.25} Fe _{0.6} Co _{0.15} Al _{0.25} O _{3-δ} (v) La _{0.8} Sr _{0.2} Fe _{0.8} Co _{0.2} O _{3-δ} / γ - AlO(OH) (vi) 0.5 wt% La _{0.8} Sr _{0.2} Fe _{0.8} Co _{0.2} O _{3-δ} . δ / γ -AlO(OH)	(i)-(vi) none	(i)-(vi) 0.1 (with 0.4 g of SiO ₂)	(i)-(vi) O ₂ 0.1	(i)-(vi) CH ₄ 0.1	(i)-(vi) 600	(i)-(vi) B ((ii),(vi) TGA)	(i)-(vi) 0-50	(i)-(vi) X	(ii),(vi) in-situ XRD	107
(i) NiO/MgO (ii) NiO-Cr ₂ O ₃ /MgO (iii) NiO-MgO (iv) NiO-Al ₂ O ₃ -MgO (v) NiO-CaO-MgO (vi) NiO-Cr ₂ O ₃ -MgO (vii) NiO-Fe ₂ O ₃ -MgO (viii) NiO-Co ₃ O ₄ -MgO	(i) SiO ₂ ,Al ₂ O ₃ ,MgO,TiO ₂ La ₂ O ₃ ,ZrO ₂ ,CeO ₂ ,Y ₂ O ₃	0.1,0.5	(i)-(viii) O ₂ 0.25	(i)-(viii) CH ₄ 0.25	(i)-(viii) 600-800	B (and TGA)	(i)-(viii) 10	(i)-(viii) 10 mins for reduction step	(ii) XRD,XPS,TPO	108
(i) 18 wt% NiO (ii) 21 wt% NiO	(i) α -Al ₂ O ₃ (ii) γ -Al ₂ O ₃	(i),(ii) X	(i),(ii) O ₂ 0.15	(i),(ii) 1-10 bar-CH ₄ 0.05-0.5 H ₂ O 0.2	(i),(ii) 800-900	SFB (and TGA)	X	(i),(ii) ~140 mins	(i),(ii) density tests,crushing strength,SEM,EDS, XRD,BET	109
18 wt% NiO	Al ₂ O ₃	(i) 40 (ii) 80	(i),(ii) air 0.21	(i),(ii)	(i),(ii) 600 or	(i),(ii) B (and	6,12	(i),(ii) ~85 mins	(i),(ii) X	110

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				$C_{0.316}H_{0.645}O_{0.0385}$ $\sim 6 \times 10^{-4}$ with H_2O $\sim 0.06-0.13$	700	TGA)				
NiO	(i) $NiAl_2O_4$ (ii) $NiAl_2O_4$ with $MgAl_2O_4$	65000	air 0.21	$CH_4 \sim 0.98$	750-900	CFB	X	X	X	111
Ce-Fe-O (7:3)	None	1.8	air 0.21	CH_4 1.0	600-900	B,TGA	5	2130-2300 s	SEM,XRD,XPS	112
60 wt% NiO	40 wt% $NiAl_2O_4$	0.2	O_2 0.211 / Ar	CH_4 0.092 with H_2O 0.03	800	B	15	10 mins	SEM	113
(i) CeO_2 (ii) Ce-Fe	(i),(ii) none	(i),(ii) 1.8	(i),(ii) air 0.21	(i),(ii) CH_4 1.0	(i),(ii) 850	(i),(ii) B	(i),(ii) 10	(i),(ii) 13 or 16 mins for reduction step	(i),(ii) XRD,XPS,TPR	114
$LaFeO_3$	none	0.1	O_2 0.1	CH_4 0.1	780-900	B	5	6 mins	SEM	115

^a B is fixed bed, FB fluidised bed, BFB is batch fluidised bed, CFB is circulating fluidised bed, SFB is semicontinuous fluidised bed and TGA is thermogravimetric analysis; ^b SEM is scanning electron microscopy, TEM is transmission electron microscopy, TPO/R is temperature programmed oxidation/reduction, XRD is X-ray diffraction, XPS is X-ray photoelectron spectroscopy and BET is Brunauer-Emmett-Teller method; a,b,c indicate different sets of reactor conditions employed; X not given

Cite this: DOI: 10.1039/c0xx00000x

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3. Membrane processes

In this part of the review, work published in the open literature is summarised into three tables followed by research highlights in which a number of specific points are raised and discussed. Table 4 presents work in which water-splitting^{ix} has been reported¹²⁶⁻¹⁴¹ as part of overall water-gas shift, reforming of methane and ethene production from ethane. Table 5 summarises syngas production from methane¹⁴²⁻²⁰⁷ and extends the review in 2004 by Thursfield and Metcalfe¹²⁵. Table 6 summarises syngas production from other hydrocarbon sources²⁰⁸⁻²²². A recent excellent review by Dong *et al.*⁵ has presented a broad range of process applications for electroceramic OTMs e.g., oxidative coupling of methane (OCM) and electroceramic proton conductors for hydrogen production. This review will complement that work by providing a detailed analysis of one application: that of OTMs for hydrogen production.

The water-splitting work, presented in Table 4^x, is a recent avenue of investigation comprising of a small number of publications which are presented chronologically. Hydrogen production studies from the partial oxidation of methane to synthesis gas are organised in Table 5 by composition of the oxide membrane materials. The first section of this table lists single phase membranes and the second section composite membranes. Table 6, 'Hydrogen production from hydrocarbon sources other than methane', reports work in which hydrogen and a mix of hydrocarbons and carbon oxides are produced. The majority of this work is concerned with increasing the hydrogen content in coke-oven-gas feeds. Specifically, for this work, an additional table column is used to report the enhancement in hydrogen content where possible.

Listed in the three tables under appropriate headings are at-a-glance salient operating conditions employed in each study. These include; the composition of the membrane material, membrane geometry and wall thickness, composition of any catalyst(s) employed, the feed composition on the oxygen permeate side of the membrane, the nature of the oxidant supply and operating temperature range. The highest hydrogen production rate is given for each citation, otherwise, where possible, it has been calculated from the provided experimental

details. In the event that authors have stated a volumetric hydrogen production rate without being specific about the temperature and pressure to which this refers we have assumed standard ambient temperature and pressure (STP, 25°C and 1atm) is applicable. Also included are aspects of membrane operation that are equally important but rarely reported in full, if at all. These include (i) whether a material balance was reported (ii) duration of operation and (iii) quantification of trans-membrane leaks. Concerning the first point, it would seem obvious that a material balance should be a part of any published study. However it is rarely comprehensively reported and may not address errors and uncertainties. An oxygen balance, for example, would characterise the oxygen permeation under operating conditions and confirm that the oxidation reaction is a direct result of permeation rather than a transient reaction of the permeate-side feed gas e.g., carbon monoxide, with the structural oxygen at the membrane surface in the absence of membrane reoxidation. This can only be done if gas analysis is performed on both sides of the membrane i.e., monitoring of oxygen consumption on one side and simultaneously the products on the permeate side. In the majority of the reported studies gas analysis is only performed on the permeate-side exit stream. Another common shortcoming is omission of the duration of operation. If the end goal of these efforts is transfer of technology to industry, then reporting the longevity of the membranes under typical (severe) operating conditions is critical. This leads to the third point; few articles report in full the rate of trans-membrane leaks, statements such as "no leakage was found" are inadequate as a minimum possible detectable leak rate should be reported in such a case.

Reporting the operating temperature in studies employing cold-sealed long tubular and microtubular membranes presents the problem of determining the temperature at which oxygen permeation is occurring. It is often assumed that the membrane operating temperature is the same as the furnace set-point temperature. However the axial temperature profile along the membrane complicates matters as the true active membrane area is difficult to calculate.

It is interesting to note that the majority of studies involving water-splitting do not report water conversion. The experimental section of these publications do not provide instrument details, e.g., of a hygrometer for measuring water content in the gas stream or simple chilled collection pot for estimating the water produced over integral times. Although reducing gas conversions are often stated, there is usually no statement on whether the membrane was operated in co-current or counter-current flow, or indeed any mention of flow patterns within the membrane module. Consequently, if operated at high conversion, the membrane system is inadequately described.

^{ix} Here the term water-splitting is used to refer to a membrane process where only water is fed to one side of the membrane. This water is split to produce hydrogen as a result of a chemical driving force across the membrane

^x The symbolism used in the tables is as that employed by the cited authors e.g., Ni/Al₂O₃, NiO/Al₂O₃ and Ni/γ-Al₂O₃ have been used to denote the employed dispersed nickel catalyst supported on alumina and O_x or O_{3-δ} have been used to describe the nominal oxygen stoichiometry in the formula for the mixed metal oxide membrane material.

Cite this: DOI: 10.1039/c0xx00000x

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Table 4 Hydrogen from water-splitting using oxygen transport membranes

Oxide system	Membrane geometry	Membrane thickness	Catalyst	Gas composition(s)		Temperature range	H ₂ production rate	Longest reported operation period	Leak detection method reported/leak quantified	Material balance reported C carbon H hydrogen O oxygen	Post op' analysis ^d	ref
							per membrane unit area ^a					
				<i>p</i> H ₂ O	<i>p</i> Sweep							
		mm		atm	atm	degC	μmol cm ⁻² s ⁻¹	hr				
0.9ZrO ₂ -0.1CaO	COE ^b tube	X	none	0.20	CO-CO ₂ 0.5-0.5	1400-1800	X	X	X	X	X	126
0.9ZrO ₂ -0.1CaO	COE ^b tube	X	none	0.20	(i) CO-CO ₂ mixes (ii) Ar 1.0	1500-1800	~2.2 ^c	X	X	X	X	127
(ZrO ₂) _{0.8} -(TiO ₂) _{0.1} -(Y ₂ O ₃) _{0.1}	COE ^b tube	2	none	0.17	H ₂ -CO ₂	1600, 1683	0.4	X	“no leakage was found”	X	X	128
CeO ₂ -Gd-NiO	disk	0.1-1.5	none	0.03-0.49	(i) H ₂ 0.04-0.8 (ii) CH ₄ 0.05	700-900	4.1	X	X	X	X	129
CeO ₂ -Gd-Ni CeO ₂ -Gd-NiO	disk	0.1-0.36	none	0.49	H ₂ 0.04-0.80	500-900	6.8	X	X	X	X	130
BaCo ₃ Fe ₇ Zr _{1-<i>x-y</i>} O _{3-δ}	microtube	0.17	Ni/Al ₂ O ₃	0.05-0.75	CH ₄ 0.01-0.10	800-950	3.4	X	X	X	X	131
BaCo ₃ Fe ₇ Zr _{1-<i>x-y</i>} O _{3-δ}	microtube	0.17	(i) none (ii) porous BaCo ₃ Fe ₇ Zr _{0.9-<i>x-y</i>} Pd _{0.1} O _{3-δ} surface layer	(i)-(ii) 0.75	(i)-(ii) CH ₄ 0.20	(i)-(ii) 800-950	(i) 0.47 (ii) 1.4	(i)-(ii) X	(i)-(ii) pressure test to 5 atm at 25°C & no trans-membrane N ₂ at 800-950°C	(i)-(ii) X	SEM STEM EDS	132
BaCo ₃ Fe ₇ Zr _{1-<i>x-y</i>} O _{3-δ}	microtube	0.17	none	0.75	C ₂ H ₆ 0.075 , 0.20	700-800	0.6	100 at 800°C	“gas-tight after 100 hrs”	X	SEM EDS	133
BaCo ₃ Fe ₇ Zr _{1-<i>x-y</i>} O _{3-δ}	microtube	0.17	Ni/Al ₂ O ₃	0.75	CH ₄ 0.04	850-950	2.2	X	O ₂ , N ₂ < 10 ⁻⁵ atm by GC	X	X	134
La _{0.3} Sr _{0.7} FeO _{3-δ}	disk	3	none	X	CO X	860	0.01	20 at 860°C	no trans-membrane Ar and He detected	X	X	135
La _{0.7} Sr _{0.3} FeO _{3-δ}	disk	1-3	none	0.025	CO X	900	0.04	8 at 900°C	no trans-membrane Ar and He detected	X	X	136
La _{0.7} Sr _{0.3} Cu _{0.2} Fe _{0.8} O _{3-δ}	(i) disk (ii) thin film	(i) 0.33-1.72 (ii) 0.05	(i) Pt and none (ii) Pt	(i)-(ii) 0.03-0.79	(i)-(ii) H ₂ 0.8	(i)-(ii) 600-900	(i) ~1.4 (ii) 7.8	(i)-(ii) X	no trans-membrane He detected	(i)-(ii) X	(i)-(ii) SEM	137
La _{0.7} Sr _{0.3} Cu _{0.2} Fe _{0.8} O _{3-δ}	thin film	0.022	none	0.03-0.49	(i) CO 0.99 (ii) CO-CO ₂ 0.5-0.5 [(i)-(ii) simulated coal-gasification] (iii) H ₂ 0.8	(i)-(iii) 600-900	(i) 3.2 (iii) ~6.8	X	trans-membrane He detected	X	(i)-(iii) X	138
(i)La _{0.7} Sr _{0.3} Cu _{0.2} Fe _{0.8} O _{3-δ} (ii) BaFe _{0.9} Zr _{0.1} O _{3-δ}	(i) supported tubular thin film (ii) disk	(i) 0.03 (ii) 1.6	(i)-(ii) none	(i) 0.49 (ii) 0.03-0.49	(i) CO 0.995 CO-CO ₂ 0.5-0.5 CO-CO ₂ 0.25-0.75 (ii) CO ₂ 0.8 / CO 0.8	(i) 500-900 (ii) 600-900	(i) 13.3 (ii) 0.2	(i) 80 (ii) X	(i)-(ii) trans-membrane He detected	(i)-(ii) X	(i)-(ii) SEM	139
SrFeCo _{0.5} O _x	(i) disk (ii) thin film	(i) 0.23-1.76 (ii) 0.02	(i)-(ii) none	(i)-(ii) 0.49	(i)-(ii) H ₂ 0.8	(i)-(ii) 900	(i) 11.9 (ii) 4	(i)-(ii) X	(i)-(ii) X	(i)-(ii) X	(i)-(ii) X	140

$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$	microtube	0.25	none	0.07	CH_4 0.05	900	0.05 ^c	260 & 400 at 900°C	10 ⁻⁴ atm O_2 & trans-membrane CH_4 monitored by GC	C, O,	XRD, SEM, EDS	141
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^a where necessary derived from volumetric flux data and assuming STP ; ^b closed at one end ; ^c membrane area not given i.e., $\mu\text{mol s}^{-1}$; ^d SEM scanning electron microscopy, XRD X-ray diffraction, EDS energy dispersive X-ray spectroscopy, STEM scanning tunnelling electron microscopy ; X not given

Table 5 Syngas from methane using oxygen transport membranes

Oxide system	Membrane geometry	Membrane thickness	Catalyst	Gas composition(s)		Temperature range	Highest reported H ₂ production rate per membrane unit area ^a	Longest reported operation period	Leak detection method reported/leak quantified	Material balance reported C carbon H hydrogen O oxygen	Post op' analysis ^c	ref
				<i>pOxidant</i>	<i>pCH₄</i> ^b							
				mm	atm	atm	degC	μmol cm ⁻² s ⁻¹	hr			
single membrane material												
Ba _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O _{3-δ}	disk	1-2	LiLaNiO _x /Al ₂ O ₃	air 0.21	25 mol% at 5 atm	850	X	40 at 850°C and 5 atm	X	X	XRD, SEM,EDS	142
Ba _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O _{3-δ}	disk	1.5	Ni/ZrO ₂	air 0.21	0.50	750-850	X	X	X	X	X	143
Ba _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O _X	(i) disk (ii)asymmetric disk	(i) ~2.3 (ii) ~2.3	(i)-(ii) 0.43 wt% Pt/ZrO ₂ & 0.40 wt% Pt/CeZrO ₂ (17.5% CeO ₂)	(i)-(ii) air 0.21	(i)-(ii) 0.40 & CO ₂ at 0.40	(i)-(ii) 800	(i)-(ii) X	(i)-(ii) 14 at 800°C	(i)-(ii) pressurised He at 800°C monitored	(i)-(ii) C,H,O	(i)-(ii) XRD, SEM,EDS	144
(i) Ba _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O _{3-δ} (ii) BaCo _{0.4} Fe _{0.4} Zr _{0.2} O _{3-δ}	(i)-(ii) disk	(i)-(ii) X	(i)-(ii) LiLaNiO _x /Al ₂ O ₃ & CoO from membrane	(i)-(ii) air 0.21	(i)-(ii) 0.50	(i)-(ii) 850	(i)-(ii) X	(i)-(ii) 50 at 850°C	(i)-(ii) X	(i)-(ii) X	(i) XRD, SEM,EDS (ii) X	145
(i) Ba _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O _{3-δ} (ii) SrFeCo _{0.5} O _x	(i)-(ii) disk	(i) 0.4 (ii) 2.2	(i)-(ii) 0.43 wt% Pt/ZrO ₂ & 0.42 wt% Pt/CeZrO ₂	(i)-(ii) air 0.21	(i)-(ii) 0.40 & CO ₂ at 0.40	(i)-(ii) 800	(i)-(ii) X	(i)-(ii) 30 at 800°C	(i)-(ii) trans-membrane N ₂ from air side, <0.3%	(i)-(ii) O	(i)-(ii) X	146
(i) Ba _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O _{3-δ} (ii) SrFeCo _{0.5} O _x	(i)-(ii) disk	(i)-(ii) ~2	(i)-(ii) 0.50 wt% Pt/ZrO ₂ & (i)-(ii) 0.40 wt% Pt/CeZrO ₂	(i)-(ii) air 0.21	(i)-(ii)0.40 & CO ₂ at 0.40	(i)-(ii) 800	(i)-(ii) X	(i)-(ii) 14 at 800°C	(i)-(ii) X	(i)-(ii) calculated material balance ±2%	(i)-(ii) X	147
BaCe _{0.15} Fe _{0.85} O _{3-δ}	disk	(i) 1.0 (ii) 1.5	(i)-(ii) LiLaNiO _x /Al ₂ O ₃	(i)-(ii) air 0.21	(i)-(ii) 0.16-0.35	(i) 750-950 (ii) 850	(i)-(ii) X	(i) 140 at 850°C (ii) 160 at 850°C	X	X	XRD, SEM,EDS	148
BaCe _{0.1} Co _{0.4} Fe _{0.5} O _{3-δ}	disk	1.0	LiLaNiO _x /Al ₂ O ₃	air 0.21	1.0	750-950	X	1000 at 875°C	X	X	SEM	149
BaCo _{0.7} Fe _{0.2} Ta _{0.1} O _{3-δ}	disk	0.7-1.6	Ni based	air 0.21	~0.5	800-950	X	400 at 900°C	X	X	SEM,EDS	150
BaCo _{0.7} Fe _{0.2} Nb _{0.1} O _{3-δ}	disk	1	2 wt% Pt,Rh,Ru/MgAlO _x Co from membrane	air 0.21	1.0	900	X	300 at 900°C	X	H ₂ O	BET,TEM	151
BaCo _x Fe _y Zr _z O _{3-δ} (X+Y+Z=1)	microtube	0.1-0.2	Ni based	air 0.21	1.0	825-925	X		trans-membrane N ₂ at 25°C	H, O	X	152
BaCo _x Fe _y Zr _z O _{3-δ} (X+Y+Z=1)	microtube	X	Ni based	air 0.21	0.9 & 0.1 H ₂ O	825-925	26.5 ^c	~300 at 875°C	X	X	X	153
BaCo _x Fe _y Zr _z O _{3-δ} (X+Y+Z=1)	microtube	0.1-0.2	(i) none (ii)Ni based	(i)-(ii) air 0.21	(i)-(ii) 0.10-0.50	(i)-(ii) 700-925	(i)-(ii) X	(i)-(ii) X	(i)-(ii) X	(i)-(ii) X	(i)-(ii) X	154
Ba(Co,Fe,Zr) O _{3-δ}	microtube	X	Ni based	air 0.21	1.0 & H ₂ O	825-925	X	X	X	X	X	155
Ba(Co,Fe,Zr) O _{3-δ}	microtube	0.16	Ni based	air 0.21	0.25-0.50 0.25-	865	X	76 at 865°C	X	X	HR-TEM,	156

[Type text]

					0.50 with 0.3,0.45 H ₂ O 0.01-0.05	850 750-900		65 at 850°C 40 cycling from 750 to 900 105 at 900°C	trans-membrane N ₂ (at 25°C?) trans-membrane N ₂ at 25°C (i)-(ii) X	Calculated C, O and H ₂ O X	SEM,EDS X	
Ba _{0.6} Sm _{0.4} Co _{0.2} Fe _{0.8} O _{3-δ}	disk	~ 0.8	1 wt% Rh/MgO	air 0.21			X					157
Ba _{0.5} Sr _{0.5} Fe _{0.8} Zn _{0.2} O _{3-δ}	X	X	none	X	0.50	900	X					158
La _{0.4} Ba _{0.6} Fe _{0.8} Zn _{0.2} O _{3-δ}	disk	(i) 0.5 (ii) 1.0	(i)-(ii) Ni based	(i)-(ii) air 0.21	(i) 0.05-1.0 (ii) 0.05-0.28	(i)-(ii) 800- 950	(i)-(ii) X	(i) X (ii) 500 at 950°C		(i)-(ii) X	(i) X (ii) XRD	159
(La _{0.5} Ba _{0.3} Sr _{0.2})(Fe _{0.6} In _{0.4})O _{3-δ}	disk	0.2	10 wt% Ni/CeO ₂	air 0.21	0.10	800-1000	40.9	100 at 1000°C	X	X	X	160
YBa ₂ Cu ₃ O _{7-x}	disk	1.0-1.4	Ni/ZrO ₂	air 0.21	0.06	800-900	X	5 at 875°C	trans-membrane N ₂ from air side, <5%	X	SEM,EDS	161
YBa ₂ Co ₂ Cu _{3-x} O _{7-δ} (0<x<0.3)	disk	1.0-1.4	Ni/ZrO ₂	air 0.21	0.06	875, 900	X	5 at 875°C	X	X	SEM	162
Ca _{0.8} Sr _{0.2} Ti _{0.7} Fe _{0.3} O _{3-δ}	disk	0.5	Ni/Ca _{0.8} Sr _{0.2} Ti _{0.9} Fe _{0.1} O _{3-δ} & La _{0.6} Sr _{0.4} CoO ₃	air 0.21	0.4	900	1.9	~7 at 900°C	X	X	X	163
Ca _{0.8} Sr _{0.2} Ti _{0.7} Fe _{0.3} O _{3-δ}	disk	0.5	Ni/Ca _{0.8} Sr _{0.2} Ti _{0.9} Fe _{0.1} O _{3-δ} & La _{0.6} Sr _{0.4} MnO ₃	air 0.21	0.1	900	1.4	~3 at 900°C	X	X	X	164
Ca _{0.8} Sr _{0.2} Ti _{0.7} Fe _{0.3} O _{3-δ}	disk	(i) 0.043 (ii) 0.068 (iii) 0.5	(i)-(iii) Ni/Ca _{0.8} Sr _{0.2} Ti _{0.9} Fe _{0.1} O _{3-δ} & La _{0.6} Sr _{0.4} CoO ₃	(i)-(iii) air 0.21	(i)-(iii) 0.1	(i)-(iii) 800- 950	(i) 6.8 (ii)-(iii) X	(i) ~7 over 800- 950°C (ii)-(iii) X	(i)-(iii) trans- membrane N ₂ from air side	(i)-(iii) X	(i)-(iii) X	165
La ₂ Ni _{0.9} Co _{0.1} O _{4+δ} La ₂ NiO _{4+δ} support	disk	0.13 1.20	Ni ⁰ from support	air 0.21	0.10	800-950	X	80 at 850°C	trans-membrane N ₂ from air side	C ±5%	XRD, XPS	166
La ₂ Ni _{0.9} Co _{0.1} O _{4+δ} La ₂ NiO _{4+δ} support	disk	0.88 0.12	Ni ⁰ from support	air 0.21	0.08-0.14	800-950	5.4	125 at 850°C	trans-membrane N ₂ from air side	C ±5%	XRD, XPS	167
(La _{0.6} Sr _{0.4})(Ga _{0.8} Mg _{0.05} Co _{0.15})O _{3-δ} with LaCeO ₂ and 50 wt% La _{0.6} Sr _{0.4} Co _{0.2} Fe _{0.8} O _{3-δ} ~ 50 wt% (La _{0.6} Sr _{0.4})(Ga _{0.8} Mg _{0.05} Co _{0.15})O _{3-δ} layer	disk	0.008-0.01	Ni-LaCeO ₂ layer	air 0.21	1.0	750	2.4	24 at 750°C	trans-membrane N ₂ from air side, <1%	X	SEM,EDS	168
La _{0.3} Sr _{0.7} Co _{0.3} Ga _{0.2} O _{3-δ}	disk	0.95	porous Pt layer	air 0.21	0.5	850-950	X	X	trans-membrane N ₂ from air side	C	SEM,EDS,XRD	169
La _{0.7} Sr _{0.3} Ga _{0.6} Fe _{0.4} O _{3-δ}	disk	(i)-(ii) 1.7 (iii) ~ 2	(i) La _{0.6} Sr _{0.4} CoO _{3-δ} (ii) La _{0.6} Sr _{0.4} CoO _{3-δ} & NiO (iii) La _{0.6} Sr _{0.4} CoO _{3-δ} & NiO/NiAl ₂ O ₄	(i)-(iii) air 0.21	(i)-(iii) 1.0	(i)-(iii) 850	X	(i)-(iii) 1.5 at 850°C	X	X	X	170
La _{0.5} Sr _{0.5} FeO _{3-δ}	(i) disk (ii) tubular	(i) 1.9 (ii) 0.9	(i)-(ii) 10 wt% NiO/Al ₂ O ₃	(i)-(ii) air 0.21	(i)-(ii) 1.0	(i)-(ii) 900	(i)-(ii) X	(i)-(ii) 250 at 900°C	(i) trans- membrane N ₂ ≤ 1% (ii) trans- membrane N ₂ ≤ 0.1%	(i)-(ii) C ±3%	(i) X (ii) XRD	171
La _{0.5} Sr _{0.5} FeO _{3-δ}	tubular	1	10 wt% NiO/Al ₂ O ₃	air 0.21	1.0	850,900,950	X	7500 at 850°C	trans-membrane N ₂ from air side	X	EDS,XRD	172
La _{0.8} Sr _{0.2} Fe _{0.7} Ga _{0.3} O _{3-δ}	COE ^d tube	~ 0.7	La _{0.8} Sr _{0.2} Fe _{0.7} NiO _{3-δ}	air 0.21	1.5 & 1.5 H ₂ O	900	X	142 at 900°C	no leak detected	C ±5%	SEM,EDS	173
La _{0.5} Sr _{0.5} Fe _{0.8} Ti _{0.2} O _{3-δ}	tubular	0.36±0.02	“catalyst” on MO	air 0.21	0.05	800-1000	X	X	X	X	SEM	174
La _{0.6} Sr _{0.4} Ti _{0.3} Fe _{0.7} O ₃ (supports are same material)	(i) disk (ii) disk (iii) porous support (iii) coated on	(i) 2.0 (ii) 0.05 on (iii) 0.05-0.1	(i)-(iii) La _{0.5} Sr _{0.5} CoO ₃ & NiO (iii) La _{0.5} Sr _{0.5} CoO ₃	(i)-(iii) air 0.21	(i)-(iii) 1.0	(i)-(iii) 900- 1000	(i) 3.7 (ii) 8.4 (iii) 19.0	(i)-(ii) X (iii) 3 at 1000°C	(i)-(ii) X (iii) no trans- membrane N ₂ leak detected at	H	X	175

[Type text]

	tubular multi-channel support		& NiO- La _{0.6} Sr _{0.4} Ti _{0.3} Ni _{0.1} Fe 0.7O ₃					0.2 MPa				
La _{0.6} Sr _{0.4} Ti _{0.3} Fe _{0.7} O ₃ (supports are same material)	(i) symmetric film on 2.5 mm thick porous disk support (ii) disk (iii) asymmetric disk film on 0.4,1.5,2.5 disk support	(i) 0.05 (ii) 2.0 (iii) 0.07	(i)-(iii) NiO & La _{0.6} Sr _{0.4} CoO ₃	(i)-(iii) air 0.21	(i)-(iii) 1.0	(i)-(iii) 1000	(i) 24.6 ° (ii) 11.7 ° (iii) 56.4 °	(i) 2.5 at 1000°C (ii-iii) X	(i)-(iii) negligible trans-membrane N ₂ from air side	(i)-(iii) C	(i)-(iii) X	176
La _{0.7} Sr _{0.3} Ga _{0.6} Fe _{0.4} O ₃ (supports are same material)	film on 0.32,0.38 0.59,0.72 & 2.5 mm porous disk supports		NiO & La _{0.6} Sr _{0.4} CoO ₃	air 0.21	1.0	1000	46.8°	X	negligible trans-membrane N ₂ from air side	C	X	176
(i) La _{0.6} Sr _{0.4} Ti _{0.3} Fe _{0.7} O _{3-δ} (ii) La _{0.6} Sr _{0.4} Ti _{0.1} Fe _{0.9} O _{3-δ}	(i) disk (ii) disk	(i) 0.1,0.2,0.3,0.5 (ii) 0.5	(i)-(ii) La _{0.5} Sr _{0.5} CoO ₃ & NiO-Ce _{0.8} Sm _{0.2} O ₂	(i)-(ii) air 0.21	(i)-(ii) 1.0	(i)-(ii) 900	(i)-(ii) X	(i)-(ii) 10 at 900°C	(i)-(ii) no leak detected	(i)-(ii) X	(i)-(ii) X	177
La _{0.6} Sr _{0.4} Co _{0.2} Fe _{0.8} O _{3-δ}	microtube	0.25	none	air 0.21	0.02	860	X	~80 at 860°C	N ₂ ~1%	C ±10-15%	X	178
SrCo _{0.8} Fe _{0.2} O _{3-δ} - 1,3,5,10 wt% doped Al ₂ O ₃	disk	1.44	4.77 wt% NiO/Al ₂ O ₃	air 0.21	0.14	800-950	X	500 at 850°C	trans-membrane N ₂ from air side	X	SEM	179
SrCo _{0.8} Fe _{0.2} O _{3-δ} - 3 wt% doped Al ₂ O ₃	tubular	0.60	17.5 wt% NiO/Al ₂ O ₃	air 0.21	0.60 & 0.12 H ₂ O	750-900	X	162 at 850°C	trans-membrane N ₂ from air side	X	XRD	180
SrCo _{0.8} Fe _{0.2} O _{3-δ} - 3 wt% doped Al ₂ O ₃	tubular	0.45	NiO/Al ₂ O ₃	CO ₂ 0.20-0.50	0.05-0.15	850-950	X	65 at 900°C	X	C ±5%	X	181
SrCo _{0.8} Fe _{0.2} O _{3-δ} - 3,5,7,9 wt% doped SrAl ₂ O ₄	disk	1.00	none	air 0.21	0.22	750-950	22.2	1200 at 850°C	trans-membrane N ₂ from air side	C ±5%	XRD, SEM	182
SrCo _{0.4} Fe _{0.5} Zr _{0.1} O _{3-δ}	disk	1.50	4.77 wt% NiO/Al ₂ O ₃	air 0.21	0.14	800-950	X	X	trans-membrane N ₂ from air side	X	X	183
SrCo _{0.4} Fe _{0.5} Zr _{0.1} O _{3-δ}	disk	1.5	4.77 wt% NiO/Al ₂ O ₃	CO ₂ 0.20	0.05	850-950	~3.5	33 at 900 °C	trans-membrane Ar from CH ₄ side	C ±5% & O	X	184
SrCo _{0.4} Fe _{0.5} Zr _{0.1} O _{3-δ}	disk	1.5	Ni/γ-Al ₂ O ₃ and Pd/ SrCo _{0.4} Fe _{0.5} Zr _{0.1} O _{3-δ}	CO ₂ 0.20	0.1	850-950	X	40 at 900 °C	trans-membrane Ar from CH ₄ side	C ±5% & O	TPD (on catalyst)	185
SrCo _{0.4} Fe _{0.5} Zr _{0.1} O _{3-δ} and porous SrCo _{0.4} Fe _{0.5} Zr _{0.1} O _{3-δ} layer	disk	1.50 (layer, 0.01)	none	CO ₂ 0.20-0.50	0.05-0.15	800-950	X	120 at 900°C	X	X	XRD, SEM	186
SrCo _{0.4} Fe _{0.5} Zr _{0.1} O _{3-δ} and porous SrCo _{0.4} Fe _{0.5} Zr _{0.1} O _{3-δ} layer	disk	1.30	17.5 wt% NiO/Al ₂ O ₃	air 0.21	0.14	800-950	X	1032 at 850°C	X	X	XRD, SEM,EDS	187
SrFe _{0.7} Al _{0.3} O _{3-δ}	disk	1.0-1.2	Ni/Al ₂ O ₃ and porous SrFe _{0.7} Al _{0.3} O _{3-δ} layer	air 0.21	0.50	700-850	X	70 at 850°C	X	X	SEM,EDS,XRD	188
SrFe _{0.6} Cu _{0.3} Ti _{0.1} O _{3-δ}	disk	1.5	Ni-Ce/Al ₂ O ₃	air 0.21	1.0	850	X	X	trans-membrane N ₂ from air side	X	X	189
SrFeCo _{0.5} O _x	disk	X	0.50 wt% Pt/ZrO ₂	air 0.21	0.40 & CO ₂ 0.40	800	X	14 at 800°C	trans-membrane N ₂ from air side, <0.2%	X	X	190
SrFeCo _{0.5} O _x	tube	0.75	Rh based	air 0.21	0.80	900	X	504 at 950°C	X	X	X	191
SrFeCo _{0.5} O _x	disk	1.0	(i) γ-Al ₂ O ₃ (ii) La _{0.6} Sr _{0.4} Co _{0.2} Fe _{0.8} O _{3-δ} (iii) 10 wt% NiO/γ-Al ₂ O ₃	(i)-(iii) O ₂ 0.20 in Ar	(i)-(iii) 1.0	(i)-(iii) 810-910	(i)-(iii) X	(i)-(iii) X	(i)-(iii) trans-membrane He or Ar at 950°C	(i)-(iii) X	(i)-(iii) SEM, XRD	192

(i) SrFe _{0.7} Al _{0.3} O _{3-δ} (ii) La _{0.3} Sr _{0.7} Co _{0.8} Ga _{0.2} O _{3-δ} (iii) La ₂ Ni _{0.9} Co _{0.1} O _{4+δ}	(i)-(iii) disk	(i) 0.95 (ii) 0.95 (iii) 0.60	(i) porous Pt layer & 0.5 wt% Pt/SiO ₂ & porous SrFe _{0.7} Al _{0.3} O _{3-δ} layer (ii) porous Pt layer (iii) 50:50 wt% porous La ₂ Ni _{0.9} Co _{0.1} O _{4+δ} /Pt layer	(i)-(iii) air 0.21	(i)-(iii) 0.5	(i)-(iii) 850- 950	(i)-(iii) X	(i) 140 over 850- 950°C & (ii) 50 over 850- 950°C (iii) X	(i)-(iii) pressure tested under 3-4 atm at 25°C? for trans-membrane N ₂ from air side	(i)-(iii) X	(i) SEM, XRD (ii) XRD (iii) X	193
Ce _{0.1} Gd _{0.9} O _{1.95-δ}	plate	0.03	NiO/YSZ & Ce _{0.1} Gd _{0.9} O _{1.95-δ} - La _{0.58} Sr _{0.4} Co _{0.2} Fe _{0.8} O 3-δ	air 0.21	0.5 and 0.5 H ₂ O	833	X	X	trans-membrane N ₂ at 25°C & 833°C	X	SEM	194
<u>composite membranes</u>												
Ce _{0.9} Sm _{0.1} O _{1.95} - x vol% Mn _{0.15- 0.5y} Co _(1+0.5y) Ni _{0.5} O ₄ (5 ≤ x ≤ 25; 0 ≤ y ≤ 1)	disk	0.3	10 wt% Ni/Ce _{0.9} Pr _{0.1} O _{2-δ}	air 0.21	0.1	800-1000	X	24 at 1000°C	X	X	X	195
(Ce _{0.85} Sm _{0.15})O ₂ - 15 vol% MnFe ₂ O ₄	plate	0.135	10 wt% Ni/Ce _{0.9} Pr _{0.1} O _{2-δ}	air 0.21	1.0 with H ₂ O	900		X	X	C,H,O		196
75 wt% Sm _{0.15} Ce _{0.85} O _{1.925} - 25 wt % Sm _{0.6} Sr _{0.4} Fe _{0.7} Al _{0.3} O _{3-δ}	disk	0.5	LiLaNiO/Al ₂ O ₃ & porous Sm _{0.5} Sr _{0.5} CoO ₃ 50 wt % Sm _{0.15} Ce _{0.85} O _{1.925} layer	air 0.21	1.0	950	X	1100 at 950°C	trans-membrane N ₂ ~ 0.1% detected	X	SEM,EDS,XRD	197
Ce _{0.8} Sm _{0.2} O _{2-δ} - La _{0.8} Sr _{0.2} Cr _{1.0} O _{3-δ}	tube	0.78	(i) SrTiO ₃ (ii) SiO ₂ (iii) Ni/γ-Al ₂ O ₃	(i)-(iii) air 0.21	(i)-(iii) 1.0	(i) 800-950 (ii)-(iii) 950	(i) 0.6 (ii) 0.06 (iii) 3.6	(i) 100 at 950°C (ii)- (iii) X	(i)-(iii) X	(i)-(iii) C,H,O	(i)-(iii) X	198
Ce _{0.8} Sm _{0.2} O _{2-δ} - La _{0.8} Sr _{0.2} CrO _{3-δ}	disk	0.72	(i) La ₄ Sr ₈ Ti ₁₂ O _{38-δ} (ii) SiO ₂ (iii) Ni/γ-Al ₂ O ₃	(i)-(iii) air 0.21	(i)-(iii) 1.0	(i) 800-950 (ii)-(iii) 950	0.6	(i) 600 at 950°C (ii)-(iii) X	(i)-(iii) X	(i)-(iii) C	SEM,XRD	199
75 wt% Ce _{0.85} Sm _{0.15} O _{1.925} - 25 wt % Sm _{0.6} Sr _{0.4} FeO _{3-δ}	disk	0.6	LiLaNiO/Al ₂ O ₃ & La _{0.6} Sr _{0.4} CoO _{3-δ}	air 0.21	1.0	950	X	636 at 950°C	trans-membrane N ₂ from air side, <0.5%	X	SEM,EDS,XRD	200
60 wt% Ce _{0.8} Gd _{0.2} O _{1.9} - 40 wt % Gd _{0.2} Sr _{0.8} FeO _{3-δ}	disk	0.5	LiLaNiO/Al ₂ O ₃ La _{0.6} Sr _{0.4} CoO _{3-δ}	air 0.21	0.2, 1.0	950	X	440 at 950°C	trans-membrane N ₂ from air side, <0.1%	X	SEM,EDS,XRD	201
Ce _{0.9} Gd _{0.1} O _{2-δ} - MnFe ₂ O ₄	disk	0.01	Pr _{0.3} Ce _{0.35} Zr _{0.35} O _{2-x} - 10 wt% LaNi _{0.9} Pt _{0.1} O ₃ & Ce _{0.9} Gd _{0.1} O _{2-δ} - La _{0.8} Sr _{0.2} Fe _{1-x} Ni _x O _{3- δ} (x=0.3,0.4)	air 0.21	(i) 0.045-0.2 (ii) 0.2 & CO ₂ 0.2	(i) 880-980 (ii) 930	(i) 3.9 ° (ii) 28.9 °	(i) 100 at 950-980°C (ii) X	(i)-(ii) trans- membrane N ₂ from air side, <0.1%	(i)-(ii) C ±5%	(i)-(ii) X	202
40 vol% La _{0.8} Sr _{0.2} MnO _{3-δ} - 60 vol% YSZ	microtube	0.075	30 vol% NiO-70 vol% YSZ	air 0.21	0.1	750-950	X	1 at 750-950	trans-membrane N ₂ from air side 750-950°C at ~ 0.001% (6 nmol cm ⁻² s ⁻¹)	X	X	203
40 vol% La _{0.8} Sr _{0.2} MnO _{3-δ} - 60 vol% ScSZr (Sc ₂ O ₃) _{0.1} (ZrO ₂) _{0.9}	microtube	0.109	35 vol% NiO-65 vol% ScSZr	air 0.21	0.1	920,990 & 1060	X	1 at 920,990 & 1060°C	trans-membrane N ₂ from seals at	C	X	204

			(Sc ₂ O ₃) _{0.1} (ZrO ₂) _{0.9}						1.2 μL s ⁻¹			
(SrFe) _{0.7} (SrAl ₂) _{0.3} O ₂	disk	1.00	none	air 0.21	0.50	850-950	X	200 at 850°C	X	X	SEM	205
YSZ - Ag	tubular	~0.005-0.02	La _{0.2} Sr _{0.8} MnO _{3-δ} - Ce _{0.8} Gd _{0.2} O _{2-δ} & YSZ-Ni porous layers	air 0.21	0.3	700-900	X	X	trans-membrane N ₂ at 25°C & N ₂ at 900°C from air side	C	X	206
YSZ (450:50 wt% Pd - TiO ₂)	tubular	0.01	La _{0.2} Sr _{0.8} MnO _{3-δ} - Ce _{0.8} Gd _{0.2} O _{2-δ} & 50:50 wt% Ni-YSZ	air 0.21	0.14,0.3	623-850	X	1.5 & 3 at 850°C	X	X	X	207

^a where necessary derived from volumetric flux data and assuming STP ; ^b 1.0 atm assumed if not stated by authors ; ^c membrane area not given i.e., μmol s⁻¹ ; ^d closed at one end ; ^e SEM scanning electron microscopy, (HR-)TEM (high resolution) transmission electron microscopy, XRD X-ray diffraction, XPS X-ray photoelectron spectroscopy, EDS energy dispersive x-ray spectroscopy, STEM scanning tunnelling electron microscopy, BET surface area, TPD temperature programmed desorption ; X not given

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

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Table 6 Syngas from other hydrocarbon sources using oxygen transport membranes

Oxide system	Membrane geometry	Membrane thickness	Catalyst	Gas composition(s)		Temperature range	Highest reported H ₂ production rate per membrane unit area ^a	Max H ₂ enhancement	Longest reported operation period	Leak detection method & reported/leak quantified	Material balance reported C carbon H hydrogen O oxygen	Post op' analysis ^c	ref
				<i>p</i> Oxidant	<i>p</i> Hydrocarbon ^b								
				atm	atm		degC	μmol cm ⁻² s ⁻¹	(H _{2 out} - H _{2 in})/H _{2 in}	hr			
(i) BaCo _{0.7} Fe _{0.2} Nb _{0.1} O _{3-δ} (ii) BaCo _{0.7} Fe _{0.2} Nb _{0.1} O _{3-δ} with CeO ₂ layer (iii) BaCo _{0.7} Fe _{0.2} Nb _{0.1} O _{3-δ} with Ce _{0.8} Sm _{0.2} O _{2-δ} layer (iv) BaCo _{0.7} Fe _{0.2} Nb _{0.1} O _{3-δ} with Ce _{0.8} Gd _{0.2} O _{2-δ} layer	(i)-(iv) disk	(i) 0.6-1.4 (ii)-(iv) 1.0	(i)-(iv)Ni/Ce _{0.75} Zr _{0.25} O ₂ /Mg ₃ (Al)O	(i)-(iv) air 0.21	(i)-(iv) 1.0 COG	(i)-(iv) 725-900	(i)-(iii) X (iv) 59.6	(i)-(iii) X (iv) 74	(i) & (iv) 100 at 850°C	(i)-(iv) trans-membrane N ₂ from air side	(i)-(iv) X	(i) & (iv) SEM,EDS,XRD (ii) & (iii) X	208
Ba _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O _{3-δ}	disk	1.4	LiLaNiO/γ-Al ₂ O ₃	air 0.21	gasoline	800-950	X	X	500 at 850°C	X	X	SEM,XRD	209
BaCo _{0.7} Fe _{0.2} Nb _{0.1} O _{3-δ}	disk	1.0	Ni/Mg(Al)O	air 0.21	1.0 COG 1.0 COG with toluene	875 825-875	66.9	100	14 cycling from 875 to 825°C	X	X	SEM,TEM EDS,XRD, TG-TPR/TPO	210
BaCo _{0.7} Fe _{0.2} Nb _{0.1} O _{3-δ}	disk	1.0	9 wt% Ni/La ₂ O ₃ /γ-Al ₂ O ₃	air 0.21	1.0 COG	825-875	34.4	88	14 cycling from 875 to 825°C	N ₂ from air side	X	SEM,EDS	211
BaCo _{0.7} Fe _{0.2} Nb _{0.1} O _{3-δ}	tubular	1.2	Ni-based	air 0.21	1.0 COG	875	X	X	100 at 875°C	X	X	SEM	212
BaCo _{0.7} Fe _{0.2} Nb _{0.1} O _{3-δ}	disk	1.0	Ru-Ni/Mg(Al)O	air 0.21	1.0 COG 1.0 COG with toluene	825-875	66.3	100	14 cycling from 875 to 825°C	X	X	SEM,EDS,XRD TG-TPR/TPO	213
BaCo _{0.7} Fe _{0.2} Nb _{0.1} O _{3-δ}	disk	1.0	(i) Ni/Mg(AlO) (ii) NiLa//Mg(AlO) (iii) NiCe/Mg(AlO)	(i)-(iii) air 0.21	(i)-(iii) 1.0 COG (i)-(iii) 1.0 COG with toluene	(i)-(iii) 800-875	(i) X (ii) 68.2 ^c (iii) X	105 ^c	(i)-(iii) 20 & 14 cycling from 875 to 800°C	(i)-(iii) X	(i)-(iii) X	XRD, (i)-(iii) SEM, XRD (& TG-TPR/TPO on catalysts)	214
BaCo _{0.7} Fe _{0.2} Nb _{0.1} O _{3-δ}	disk	1.0	(i) LiNiO _x /γ-Al ₂ O ₃ (ii) LiNi 1 wt% LaO _x /γ-Al ₂ O ₃ (iii) LiNi 5 wt% LaO _x /γ-Al ₂ O ₃ (iv) LiNi 15 wt% LaO _x /γ-Al ₂ O ₃ (v) LiNi 1 wt% CeO _x /γ-Al ₂ O ₃ (vi) LiNi 5 wt% CeO _x /γ-Al ₂ O ₃ (vii) LiNi 15 wt% CeO _x /γ-Al ₂ O ₃	(i)-(vii) air 0.21	(i)-(vii) 1.0 COG	(i)-(vi) 875 (vii) 800-875	(i)-(vii) X	(i)-(vii) X	(i)-(vii) X	(i)-(vii) X	(i)-(vii) X	SEM,EDS	215
BaCo _{0.7} Fe _{0.2} Nb _{0.1} O _{3-δ}	disk	1.0	NiO/MgO	air 0.21	1.0 COG	800-900	68.2	89	100 at 875°C	trans-membrane N ₂ from air side	X	SEM,EDS,XRD TG-TPR/TPO	216
BaCo _{0.7} Fe _{0.2} Nb _{0.1} O _{3-δ}	disk	1.0	(i) none (ii) 5 wt% La ₂ O ₃ -9 wt% Ni/γ-Al ₂ O ₃ on δ-Al ₂ O ₃ layer	(i)-(viii) air 0.21	(i) & (iii) varied H ₂ , varied CH ₄ , varied CO, 1.0 COG and H ₂ -CH ₄ -CO mixes	(i) 800,850 875 (ii) 850 (iii) 800,850	(i)-(viii) X	(i)-(viii) X	(i)-(viii) X	trans-membrane N ₂ from air side	(i)-(viii) X	SEM,EDS	217

			(iii) surface Ni (iv) surface Fe (v) surface Mn,Ag,Au,Pt (vi) 5 wt% La ₂ O ₃ -9 wt% Ni/ γ -Al ₂ O ₃ (vii) surface Co (viii) Co _{0.3} Mg _{0.7} O surface layer		(ii)&(vi) varied CH ₄ (iv),(vii) & (viii) 1.0 COG (v) 0.2 H ₂	(iv) 875 (v) 800 (vi) 850 (vii) 875 (viii) 875							
BaCo _{0.7} Fe _{0.2} Nb _{0.1} O ₃₋₈	disk	1.0	(i) none (ii) Ni-based supported catalyst (iii) Ni-based catalyst film	(i)-(iii) air 0.21	(i) & (iii) varied CH ₄ , varied CO (ii) 1.0 COG	(i)-(iii) 875	(i)-(iii) X	(i)-(iii) X	(i),(iii) X (ii) 550 at 875°C	(i)-(iii) X	(i)-(iii) X	SEM,EDS	218
Ba _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O ₃	disk	1.8	(i)-(ii) LiLaNiO/ γ -Al ₂ O ₃	(i)-(ii) air 0.21	(i) C ₇ H ₁₆ (ii) simulated gasoline	(i) 750-950 (ii) 850	(i)-(ii) X	(i)-(ii) X	(i) 100 at 850°C (ii) 80 at 850°C	(i)-(ii) X	(i)-(ii) X	X	219
Ba _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O ₃	disk	1.4	LiLaNiO/ γ -Al ₂ O ₃	air 0.21	C ₇ H ₁₆	750-950	X	X X	100 at 850°C	X	X	SEM,XRD	220
Bi ₂ V _{0.8} Ta _{0.2} O _{5.5}	(i) disk polished with 800 grit SiC paper (ii) disk polished with 220 grit SiC paper	(i)-(ii) 1.5	(i)-(ii) X	(i)-(ii) O ₂ 0.2-1.0	(i) 0.01 C ₃ H ₈ (ii) 0.01 C ₃ H ₈ or 0.01 C ₃ H ₆ or 0.01 C ₂ H ₆	(i) 650 (ii) 650 & 675	(i)-(ii) X	(i)-(ii) X	(i) 0.8 at 650°C (ii) 1 at 650°C	(i)-(ii) X	(i)-(ii) X	SEM,EDS,XRD XPS ^c	221
(a) Bi ₄ Cu _{0.2} V _{1.8} O _{10.7} (b) Bi ₄ Co _{0.2} V _{1.8} O _{10.7}	(i) disk membrane (a) unpolished (ii) disk membrane (b) unpolished (iii) disk membrane (a) polished with 200 grit SiC paper (iv) disk membrane (b) polished with 200 grit SiC paper	1.7	(a)-(b) – (i)-(iv) X	(i)-(ii) air 0.21 (iii)-(iv) air 0.21, O ₂ 1.0	(i)-(ii) 0.01 C ₃ H ₆ (iii)-(iv) C ₃ H ₆ , 0.01 C ₃ H ₈ 0.01	(i)-(iv) 550- 750	(i)-(iv) X	(i)-(iv) X	(i)-(ii) 720 cycling from 650 to 700°C (iii) 1.25 at 650°C (iv) 2.2 at 700°C	(i)-(iv) X	(i)-(iv) X	SEM,XRD,LRS XPS ^c	222

^a where necessary derived from volumetric flux data and assuming STP ; ^b 1.0 atm assumed if not stated by authors ; ^c data not presented ; ^d SEM scanning electron microscopy , TEM high resolution transmission electron microscopy, XRD X-ray diffraction, XPS X-ray photoelectron spectroscopy, EDS energy dispersive X-ray spectroscopy, LRS laser Raman spectroscopy, TG-TPR/TPO thermogravimetric-temperature programmed reduction/oxidation ; COG is simulated coke oven gas ; X not given

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Oxygen transport membrane materials We consider the general requirements for the membrane oxide as in the specific applications considered below it acts in a similar role as a provider and distributor of oxygen. From Tables 4, 5 and 6 it is clear that efforts continue to be mainly focused on single phase perovskite-type mixed metal oxides containing at the A-site (i) barium and/or strontium, or (ii) the much used lanthanum and strontium combination. The employed B-site cation(s) have primarily been transition metals, particularly cobalt and iron but also group three elements such as aluminium and gallium have been incorporated. Non-perovskite oxides however are starting to attract attention. It is interesting to note that the fluorite-type $\text{Ce}_{0.1}\text{Gd}_{0.9}\text{O}_{1.95-8}$ was recently used as an OTM¹⁹⁴. Usually it is employed as an electrolyte membrane for solid oxide fuel cell applications as it possesses good ionic and low electronic conductivity. However when the bulk oxygen diffusion length is *ca* 30 μm its low electrical conductivity is sufficient to provide an oxygen flux without the necessity of electrodes and external circuitry. This electrical conductivity presumably has its origins in the $\text{Ce}^{+4} \leftrightarrow \text{Ce}^{3+}$ redox couple.

An alternative membrane strategy to the single phase oxides is the dual phase composites (mixtures of ionic and MIEC oxides or metal), a number of composite materials have been tested based on the Ce-Sm and YSZ fluorite systems (listed in the second section of Table 5). The tested membranes have generally been thicker than 30 μm , with the exception of the YSZ-Ag composite²⁰⁶. YSZ does not possess a redox centre such as $\text{Ce}^{+4} \leftrightarrow \text{Ce}^{3+}$ and so requires an electrical conductor. Composites have been proposed as alternative OTM materials to the single phase perovskite-type MIECs for long term stability reasons. However, with the exception of the 75 wt% $\text{Sm}_{0.15}\text{Ce}_{0.85}\text{O}_{1.925-25}$ wt% $\text{Sm}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.7}\text{Al}_{0.3}\text{O}_{3-8}$ system operated for 1100 hours at 950°C¹⁹⁷, the reported long term operation of the composites are not remarkable compared to the single phase perovskite-type oxide based OTMs. The composite strategy presents a number of potential problems, notably; (i) expensive noble metals are often used (ii) thermal expansion mismatch (iii) solid state reaction between the two phases and (iv) interdiffusion of cations.

Membrane geometry and architecture Most reported studies have employed the planar disk geometry because of ease of fabrication and assembly in bench scale reactor studies. A few groups have searched for improvements in performance through sophisticated membrane architectures. The microtubular membrane produced by the phase inversion technique offers the advantage of high surface area to volume ratios with thin membrane wall to reduce bulk oxygen diffusion path length. Asymmetric membrane structures can provide a significant improvement in performance; high porosity at one surface can provide a higher active surface area compared to the opposite surface. This can be used to ensure a high oxygen permeation

rate, providing sufficient oxygen to stabilise the membrane during demanding operating conditions. An example of interest is the rather complicated nanocomposite multilayer membrane design by Sadykov *et al.* in which three graded porous layers were used to support a thin composite $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-8}$ - MnFe_2O_4 OTM film onto which a foam nickel reforming catalyst was applied²⁰². The system performed reasonably well compared to single phase Ba-Sr-Co-Fe based perovskite OTMs.

In a multilayer membrane study hydrogen production was obtained at the low temperature of 750°C by using a supported thin $(\text{La}_{0.6}\text{Sr}_{0.4})(\text{Ga}_{0.8}\text{Mg}_{0.05}\text{Co}_{0.15})\text{O}_{3-8}$ membrane of *ca* 9 μm thickness¹⁶⁸. The aim was to achieve good activity at a relatively low temperature compared to that reported in other studies. While some activity was obtained, performance was hindered by the relatively low temperature. The authors did not report studies at higher temperature in order to investigate best performance.

A design akin to the tubular solid oxide fuel cell in which an electronically conducting palladium-titanium oxide belt was inserted into a trench along a partially sintered YSZ tube has been reported²⁰⁷. It was suggested that such a refractory OTM should be more stable under POM conditions but its performance was reported for only three hours.

An extruded porous multi-channel tubular support with a thin OTM coating on the outside has been reported by Kawahara *et al.*¹⁷⁵. The porous support and the OTM were fabricated from the same $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ti}_{0.3}\text{Fe}_{0.7}\text{O}_3$ perovskite-type oxide. The support structure comprised two concentric tubes with the inner tube supporting the outer with struts running the length of the tube to form channels between the two tubes. During operation, air was passed down the centre, entered the middle section comprising of the channels and contacted the outer OTM structure. This system was clearly superior to the simple disk membrane geometry of the same material, giving a hydrogen production rate almost five times higher, albeit over only three hours of operation.

Perhaps the most straight forward improvement in membrane performance is simply to reduce the thickness. The two thinnest membranes investigated were in the form of a complicated multilayer system. In one system the OTM component is 8-10 μm thick formed by drop-coating¹⁷⁶ and in the other, a multilayer system in which the OTM is a YSZ-Ag composite formed by electroless plating the silver into a porous YSZ tube providing an OTM of 5-20 μm thickness²⁰⁶.

3.1. OTM-based water-splitting

3.1.1. Early work on hydrogen production using oxygen transport membranes (1982-1995)

The equilibrium conversion for the thermal splitting of water can be exceeded if the resultant oxygen is removed from the gas

phase by permeation across an OTM. Unconverted water can be condensed and the free gas phase hydrogen readily collected. In Kroger-Vink notation, where; $V_O^{\bullet\bullet}$ denotes an oxygen vacancy at a site in the oxygen sub-lattice with a charge of +2, O_O^x denotes an oxygen occupying a site in the oxygen sub-lattice with no net charge and e^- an electron, the water-splitting reaction over a reduced membrane surface can be written as:

At the permeate side oxygen is released creating an oxygen vacancy and donating two electrons back to the crystal metal cation-oxygen network:

In order to facilitate this simultaneous ionic and electronic current, termed ambipolar conduction, metal cations of variable valance state are required to support the electronic current and mobile oxygen vacancies for the ionic current. This provides the mechanism for oxygen anion transport without the requirement of external circuitry. In this system an oxygen chemical potential gradient across the membrane provides the driving force.

The relatively small body of work, presented in Table 4, shows little use of catalysts for water-splitting or for the oxidation reaction on the oxygen-permeate membrane surface. The few studies employing catalysts have involved a nickel reforming catalyst where methane is the sweep gas^{131,134} or a porous layer of the membrane material with palladium incorporated¹³², also, a porous layer of platinum in contact with both membrane surfaces when hydrogen was used as sweep gas¹³⁷. The latter surface modification provided a significant improvement in performance compared to that of the bare membrane.

The earliest reported work for this application involved fundamental studies utilising OTMs at temperatures as high as 1800°C. At these temperatures pure ionic conductors can demonstrate sufficient electronic conductivity to allow transport of oxygen anions without electrodes or external circuitry. Using a calcia-stabilised zirconia, closed-at-one-end, tubular membrane, Cales and Baumard and Lede *et al*^{126, 127} were able to produce hydrogen, the resultant oxygen was transported to a separate compartment in order to overcome the equilibrium limitation. These pioneering studies were not focused on producing an optimised system to obtain high hydrogen production rates, but were undertaken to evaluate the feasibility of the process. They used a carbon monoxide-carbon dioxide buffer (the overall driving force would be that of the water-gas shift reaction) in the oxygen permeate chamber and also argon at high flow rates to remove the transported oxygen and thus maintain a constant oxygen chemical potential gradient across the membrane. From the oxygen flux the hydrogen production rate was calculated. The influence of the partial pressure of oxygen on the permeate side was also investigated by adjusting the carbon monoxide to carbon dioxide ratio. Although novel and of importance the work suffers from the lack of on-line gas analysis to directly detect the produced hydrogen at the outlet of the water-feed compartment. The limiting factor in performance in this early work was the low

n-type electronic conductivity of the metal oxide membranes employed. Thirteen years later the idea of employing a dual phase mixed ionic electronic conductor (MIEC) based on ZrO_2 - Y_2O_3 was taken up by Naito and Arashi¹²⁸. The workers carefully controlled the oxygen partial pressure on the permeate side by using a hydrogen-carbon dioxide buffer mix and also directly evaluated the hydrogen production rate using gas analysis. The effect of doping in 10 mol% titanium oxide into the ZrO_2 - Y_2O_3 host membrane on the hydrogen production rate was however rather modest and it became clear that advances in MIEC electroceramic materials was required.

3.1.2. Water-splitting with removal of permeate oxygen employing hydrogen as sweep gas

More recent work using cermet composites of gadolinium doped ceria (CGO) with nickel has provided an increase in hydrogen production by increasing the membrane electronic conductivity. The initial work was a proof-of-concept study in which hydrogen and also methane were used as sweep gases in the oxygen permeate side of the membrane reactor¹²⁹. A higher hydrogen production rate at significantly lower temperatures than the first studies based upon doped zirconia was reached. A log dependence of the hydrogen production rate with the hydrogen and water partial pressures was found indicating oxygen-anion diffusional limitations in the membrane; varying the thickness of the membrane verified this. An oxygen material balance was not possible as gas analysis was only performed on the water feed-side to detect hydrogen. The rate of oxygen anion formation was increased by application of a porous layer of the same cermet, increasing the rate of hydrogen production. Using nickel oxide instead of nickel in the composite produced a significant increase in the hydrogen production rate. This observation was ascribed to the observed increase in the three phase boundary length between the nickel oxide/CGO compared to nickel/CGO because of more intimate mixing of the two phases¹³⁰.

A copper-substituted, La-Sr-Fe-based, perovskite-type MIEC has attracted attention recently due to its electrocatalytic activity for oxygen reduction²²³. The material has provided an impressive rate of hydrogen production when used in the form of supported thin films with hydrogen as a permeate sweep gas^{137, 138}. It was demonstrated that thin membranes coated with a porous platinum catalyst surface layer can increase the rate of hydrogen production. The data were obtained under controlled conditions; the driving force was maintained with 0.8 atm of hydrogen as sweep gas and a high partial pressure of water was employed. Under these conditions a hydrogen production rate of *ca* 7.8 $\mu\text{mol cm}^{-2} \text{s}^{-1}$ was reported. The authors did not provide any long term studies but post operation SEM showed no fracture, development of porosity or evidence of recrystallisation at the membrane surfaces.

Also worthy of note is the performance of a 20 μm thick MIEC $\text{SrFeCo}_{0.5}\text{O}_x$ membrane which recently demonstrated a hydrogen production rate of 11.9 $\mu\text{mol cm}^{-2} \text{s}^{-1}$ ¹⁴⁰. The material undergoes a sharp phase change at *ca* 825°C with resultant drop in rate of

oxygen permeation, possibly through a process such as vacancy ordering. The performance of the thin film was less than that predicted due to concentration polarisation and surface kinetic limitations. This was partly mitigated by application of a porous layer of the membrane material.

3.1.3. Water-splitting with carbon monoxide as sweep gas (overall water-gas shift)

The water-gas shift (WGS) reaction for hydrogen production has been reported using a membrane formed from $\text{La}_{0.3}\text{Sr}_{0.7}\text{FeO}_3$ ¹³⁵. Water and carbon monoxide were fed into the two separate membrane module compartments:

Giving overall the water-gas shift reaction:

The experiment was incompletely described, e.g., the partial pressure of the inlet carbon monoxide and water is not provided. An interesting and rather surprising finding was the residual activity of the membrane following interruption of the carbon monoxide flow and switching to an inert gas. The membrane continued to produce a steadily decreasing amount of hydrogen, stabilising at a non-zero activity. The workers also investigated $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3$ using the same experimental protocol¹³⁶. The lower strontium content provides a lower oxygen vacancy concentration and therefore a lower oxygen permeation rate. A disk membrane of thickness 1 mm provided a higher oxygen flux than thicker membranes indicating bulk transport limitations for these materials. Conductivity measurements also showed that vacancy ordering occurs when the strontium doping increases beyond 0.5 in this oxide family, lowering ionic conductivity²²⁴. Direct comparison of the hydrogen production performance is not possible however as the experiments were carried out at 860°C¹³⁵ and 900°C¹³⁶. The reader should be aware of the published erratum²²⁵ to a figure presented in that work¹³⁵.

The advantage of reducing membrane wall thickness to 30 µm and using tubular geometry has been demonstrated using a supported $\text{La}_{0.7}\text{Sr}_{0.3}\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ OTM. To date, this system has provided the highest rate of hydrogen production (13.3 µmol cm⁻² s⁻¹) reported for OTM-based WGS¹³⁹.

3.1.4. Water-splitting with methane as sweep gas (overall steam reforming of methane)

Steam reforming of methane has also been demonstrated as a candidate process for OTM technology^{130-132, 134, 141}. The oxygen transported across the membrane from water dissociation is used to partially oxidise methane to synthesis gas:

Overall the process is steam reforming:

The commercially attractive hydrogen production rate of 3.4 µmol cm⁻² s⁻¹ has been achieved from this promising process using $\text{BaCo}_x\text{Fe}_y\text{Zr}_{1-x-y}\text{O}_{3-\delta}$ ¹³¹. The influence of a nickel-based reforming catalyst to accelerate the conversion of methane and to maintain a low oxygen chemical potential at the oxygen permeate-side membrane surface was demonstrated. In a later study, surface modification of this OTM with a porous $\text{BaCo}_x\text{Fe}_y\text{Zr}_{0.9-x-y}\text{Pd}_{0.1}\text{O}_{3-\delta}$ layer deposited on the methane feed side membrane surface¹³² gave a lower hydrogen production rate under similar conditions to the previous work¹³¹. However a reforming catalyst was not used in conjunction with the porous layer¹³². The surface-modified membrane was, however, superior to the unmodified reference membrane tested as part of the study¹³². The performance of the modified membrane was ascribed to a synergistic affect between cobalt and palladium; EDS indicated a degree of co-segregation of the two.

A study has provided evidence for the need for a finite time in order to establish an oxygen vacancy gradient across a $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ microtubular membrane to facilitate oxygen transport¹⁴¹. In this study an induction period of ca 30 hours was observed before the onset of water-splitting to produce hydrogen and at the same time CO_x products on the methane feed side. No such induction period has been reported in similar studies, this may be due to the low virtual oxygen partial pressure produced by the inlet feed of 0.07 atm of water giving a relatively weak driving force (from Table 4 it is apparent that higher water partial pressures from 0.2 to 0.75 atm are commonly used). Also of note is the reported 400 hours of continuous operation, the longest to date for this process reported in the open literature.

3.1.5. Water-splitting with ethane as sweep gas (overall non-oxidative dehydrogenation of ethane to ethene)

Some attention has also been given to coupling water-splitting with dehydrogenation of ethane¹³³ (and also partial oxidation of methane with nitrous oxide reduction in a dual study¹³⁴) as another possible route to hydrogen production.

3.2. Hydrocarbons for synthesis gas production

The application of MIEC OTMs for syngas production from hydrocarbon sources continues to attract attention, to-date this has primarily been directed to methane utilisation as can be seen in Table 5. This modestly exothermic reaction is suited to OTM technology as the membranes can be operated to provide a controlled and evenly distributed delivery of oxygen. On the gas-phase oxygen feed side, oxygen is incorporated into the oxygen sublattice:

the transported oxygen anions can then combine, enter the gas phase and react with, e.g., methane:

The utilisation of hydrocarbons other than methane will be discussed in Section 3.2.2.; a summary of work since 2004 is provided in Table 6.

As will be discussed later, there is also growing interest in the endothermic dry reforming of methane with carbon dioxide.

$$\Delta H_{298K}^0 = +247 \text{ kJ mol}^{-1}$$

In this process the two are co-fed into the same membrane compartment and oxygen is provided by the OTM as for the POM process. Table 5 lists five such studies since 2004^{144, 146, 147, 190, 202}.

3.2.1. Methane

Supported nickel is currently the mainstay methane reforming catalyst. Nickel is exceptionally good at cleaving the C-H bond making it the catalyst of choice. It activates the methane molecule for POM in OTM processes, and in so doing, maintains the oxygen chemical potential driving force across the OTM by ensuring that the transported oxygen is rapidly consumed. Noble metals have also been used and there is growing interest in using ceria-based oxides as catalyst supports. These supports are in the form of particles which are coated onto the membrane surface. On the oxygen feed side, perovskite-type mixed metal oxides are often used to accelerate oxygen reduction and incorporation at the membrane surface, an application that parallels SOFC systems. The constituent membrane cations may also play a role in catalysing the POM or oxygen dissociation reaction.

Post operation SEM indicated a porous layer of cobalt oxide on the methane exposed membrane surface after POM studies by Tong *et al.* using Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} and BaCo_{0.4}Fe_{0.4}Zr_{0.2}O_{3-δ} OTMs¹⁴⁵. They stated that this layer is of potential benefit as it increases surface area and acts as an additional oxidation catalyst. It has also been stated that non-segregated cobalt from the membrane may act as an oxygen dissociation catalyst although no evidence was shown to support this¹⁵¹.

Recent studies using a La₂Ni_{0.9}Co_{0.1}O_{4+δ} OTM with nickel-containing porous La₂NiO_{4+δ} disk supports¹⁶⁶ and a complicated multilayer graded disk support¹⁶⁷ have indicated that during POM, nickel from the support, corroborated by XPS, may segregate and disperse at the “atomic-scale” onto the membrane and enhance POM performance.

The possible influence of oxygen spillover from the OTM onto the reforming catalyst has been investigated using

Ba_{0.6}Sm_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} with rhodium supported on magnesium oxide¹⁵⁷. This spillover could enhance the catalyst activity and so increase the rate of methane conversion. The investigation involved varying the separation distance between the membrane surface and catalyst layer by using a plug of inert quartz wool of varying thicknesses. It was found that the supply of methane had a greater affect on oxygen permeation than variation in the adjusted distance. Replacing methane with hydrogen and carbon monoxide further increased oxygen permeation rates. It was concluded that the POM products diffused through the quartz wool and consumed the oxygen permeate at the membrane surface providing a mechanism to improve permeation and indicating that oxygen spillover played no significant role. In a similar study using a Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_x OTM with platinum supported on ceria zirconate for the dry reforming of methane with carbon dioxide, it was found that the carbon dioxide conversion was greater with intimate contact between the catalyst and OTM¹⁴⁴. It was also put forward that a synergy between the two existed in which the high oxygen flux provided by Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_x acted to stabilise the reforming catalyst through oxygen spillover by preventing reduction of Ce⁴⁺ to Ce³⁺. Evidence for the combustion reforming mechanism through temperature profile measurement employing thermocouples placed at the internal tubular membrane surface and within the reforming catalyst has been provided¹⁷². Heat was generated at the membrane surface indicating methane combustion to water and carbon dioxide with the oxygen permeate. These products then diffuse to the catalyst layer where steam and dry reforming of methane occur accompanied by a drop in temperature.

A mechanistic study using transient temporal analysis of products (TAP) has recently been undertaken with the BaCo_xFe_yZr_zO_{3-δ} (X+Y+Z=1) OTM material¹⁵⁴. Methane and ethane were pulsed over membrane fragments in the absence of gaseous oxygen to investigate intermediates and the role of lattice oxygen.

Work has recently been reported on dry reforming in which a mix of methane and carbon dioxide is fed to one side of the OTM. The process could be applied to syngas production from natural gas streams with high carbon dioxide content without the need to carry out carbon dioxide separation. The syngas from this route has a hydrogen to carbon monoxide ratio *ca* one-to-one if the methane to carbon dioxide feed ratio is one-to-one. This can be used to adjust the composition of other syngas mixes. The problem with this process is deactivation of the reforming catalyst through sintering and coke deposition as a result of the presence of carbon dioxide. Controlled supply of distributed oxygen from a SrFeCo_{0.5}O_x OTM has been shown to enhance and maintain the activity of a zirconia supported platinum reforming catalyst, although data presented was for only 14 hours of operation¹⁹⁰. Oxygen supplied by the OTM was better at methane conversion than co-feeding gas phase oxygen with the methane. No data was presented regarding product selectivity. Further work after this initial study has focused on using Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_x and SrFeCo_{0.5}O_x OTMs^{144, 146, 147}. The studies indicate that oxidation of hydrogen to water, (the hydrogen being produced by decomposition of methane on the

reforming catalyst) leads to steam reforming of methane with a drop in carbon dioxide conversion¹⁴⁴. The highest hydrogen production rate from this process has been obtained from the multilayer membrane described earlier²⁰². The rate of 28.9 $\mu\text{mol s}^{-1}$ was obtained by optimising experimental conditions but is another example of unspecified operating time and incomplete experimental details e.g., membrane surface area.

An interesting idea is to replace air with carbon dioxide as the source of oxygen. This is a challenging application as the membrane surfaces are exposed to reducing gases from the syngas produced on the methane feed-side and carbon monoxide from the carbon dioxide feed-side. This process was recently tested using $\text{SrCo}_{0.4}\text{Fe}_{0.5}\text{Zr}_{0.1}\text{O}_{3-\delta}$ ¹⁸⁴⁻¹⁸⁶ and $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ -3 wt% doped Al_2O_3 ¹⁸¹ OTMs. Efforts have so far provided a hydrogen production rate of *ca* 3.5 $\mu\text{mol cm}^{-2} \text{ s}^{-1}$ over 33 hours¹⁸⁴. The same type of OTMs, when used with air as oxidant in POM studies, have shown impressive durability, operating for over 1000 hrs and providing a hydrogen production rate of *ca* five times that when using carbon dioxide^{181, 182, 187}.

3.2.2. Syngas from other hydrocarbon sources

From Table 6 it is apparent that the majority of studies have employed coke oven gas (“COG”); a by-product generated in the production of coke from coal. This is a complicated mix comprising of; hydrogen (*ca* 54-59 mol%), methane (*ca* 24-28 mol%) carbon monoxide (*ca* 5-7 mol%), carbon dioxide (*ca* 1-3 mol%) nitrogen (*ca* 3-5 mol%), oxygen (*ca* 0.3-0.7 mol%), “other hydrocarbons” (*ca* 2-3 mol%) and hydrogen sulfide (*ca* 0.01-0.5 mol%)²¹⁰. In all of the listed COG studies a simulated COG feed has been used in which only the first four above listed components are used. Almost all of this work has involved the use of $\text{BaCo}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-\delta}$ OTMs as the work has mainly been carried out by a single research group who have exclusively used this membrane material. The syngas produced from the simulated COG is generally mixed with unconverted species such as carbon dioxide and methane. Higher hydrogen production rates are reported in these studies compared to those from the POM studies presented in Table 5 because of the high initial concentration of hydrogen in the COG feed. The highest reported hydrogen-equivalent flux from COG is *ca* 68 $\mu\text{mol cm}^{-2} \text{ s}^{-1}$ obtained using nickel-based reforming catalysts^{214, 216}.

Most of the reported studies have employed supported nickel based reforming catalysts. In addition to this, a number of studies, such as those by Cheng *et al.*²⁰⁸, have conducted trials with surface modification of the membrane to improve oxygen flux and protect the membrane. The authors used a $\text{BaCo}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-\delta}$ OTM coated with a porous layer of $\text{Ce}_{0.8}\text{Re}_{0.2}\text{O}_{2-\delta}$ (Re=Sm, Gd) on the permeate surface and on top of this porous layer a layer of $\text{Ni/Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2/\text{Mg}_3(\text{Al})\text{O}$ reforming catalyst was placed. Ceria based oxides possess good electronic and ionic conductivity and can promote the activity of catalysts that they contact. It was found that the surface modification increased the oxygen permeation and methane conversion but decreased the hydrogen selectivity due to the reaction of oxygen with hydrogen and carbon monoxide in the COG, producing

water and carbon dioxide. The membrane with the $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ layer gave better oxygen flux enhancement compared to the samarium analogue, no explanation was put forward to explain this. A comparison test using a bare membrane under identical conditions resulted in degradation compared to an OTM protected by the porous layer.

Other studies have reported the feasibility of producing hydrogen from (simulated) gasoline^{209, 219}, heptane²²⁰, ethane, propene and propane^{221, 222}. As an example study, Zhu *et al.*²⁰⁹ investigated the partial oxidation of simulated gasoline to produce hydrogen. The authors reported that a $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ OTM with a $\text{LiLaNiO}/\gamma\text{-Al}_2\text{O}_3$ reforming catalyst operated for 500 hours providing hydrogen and carbon monoxide selectivity at *ca* 90%. It was found that below 850°C ethane and ethene were produced with the syngas but were converted to syngas above 850°C. Formation of strontium and barium carbonates were found at the gasoline feed side but the bulk and oxidising surface of the membranes retained the original structure.

3.3. Membrane performance: hydrogen production rate and durability

Few workers specifically report the hydrogen production rate. The highest reported flux from POM is *ca* 41 $\mu\text{mol cm}^{-2} \text{ s}^{-1}$ obtained using $(\text{La}_{0.5}\text{Ba}_{0.3}\text{Sr}_{0.2})(\text{Fe}_{0.6}\text{In}_{0.4})\text{O}_{3-\delta}$ ¹⁶⁰. The hydrogen production rate of *ca* 56 $\mu\text{mol s}^{-1}$ for supported $\text{La}_{0.7}\text{Sr}_{0.3}\text{Ti}_{0.3}\text{Fe}_{0.7}\text{O}_3$ ¹⁷⁶ is also probably worthy of note (no membrane area was given). For the water-splitting process, the thin tubular $\text{La}_{0.7}\text{Sr}_{0.3}\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ OTM operated for 80 hours represents the highest hydrogen production to date, providing *ca* 13 $\mu\text{mol cm}^{-2} \text{ s}^{-1}$ without any surface catalyst¹³⁹.

Post operation analysis is an important part of OTM performance investigations, this commonly involves SEM, EDS or XRD which are usually employed together. These techniques often reveal the formation of small crystals on the membrane surface due to recrystallisation, the formation of either dense or porous layers on the membrane surfaces at the methane and oxygen feed sides and the development of secondary phases from the OTM material. The high barium containing OTMs are particularly susceptible to carbonate formation. Composite membranes often show evidence of solid state reaction between the component phases. Analysis can provide insight into factors that cause degradation in system performance over time and may give clues to factors giving rise to membrane failure. The information can be used to produce membranes with improved stability under operating conditions.

The emerging application of OTM based water-splitting is poorly reported regarding duration of operation. The longest reported duration is 400 hours at 900°C using microtubular $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ ¹⁴¹. However performance was most likely hindered by segregation of La_2O_3 and SrO at the water exposed membrane surface with SiO_2 contamination from the quartz module shell. This deterioration of the membrane inevitably impacts on oxygen flux as the layers will tend to hinder oxygen flux. At the methane-exposed surface, evidence for CoSO_4 was observed.

To the authors' knowledge the longest continuous OTM operation for hydrogen production (POM for syngas) thus far reported, is 7,500 hours for the perovskite-type ferrite $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ ¹⁷². Post operation XRD and EDS indicated no change in phase purity and no segregation or composition changes at the membrane surfaces from kinetic demixing. An advantage of this ferrite MIEC oxide is the absence of more easily reducible cobalt giving rise to improved stability.

The longest reported continuous hydrogen production from COG to syngas is 550 hours using $\text{BaCo}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-\delta}$ as OTM with an undefined commercial supported nickel-based reforming catalyst²¹⁸. Post operation XRD showed that the content of barium increased at the surface exposed to air and the content of cobalt increased on the surface exposed to the COG. SEM indicated that both surfaces of the membrane had become porous. Post operation XRD has revealed cobalt oxides and barium carbonate formation in most of the studies using $\text{BaCo}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-\delta}$ but with no significant changes in the bulk of the OTM.

Post operation investigation of the 75 wt% $\text{Sm}_{0.15}\text{Ce}_{0.85}\text{O}_{1.925-25}$ wt% $\text{Sm}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.7}\text{Al}_{0.3}\text{O}_{3-\delta}$ composite OTM after 1100 hours indicated no structural change at the methane-exposed membrane surface; both surfaces had retained their dense non-porous character¹⁹⁷. The authors attributed this stability to (i) the low alkaline-earth and reducible metal cation content compared to that typically found in perovskite-type OTMs (ii) the isolation of the perovskite and fluorite grains (iii) low creep and (iv) beneficial compensatory cation interdiffusion during synthesis.

4. Comparison between chemical looping and membrane processes

Some materials have been used for hydrogen production in both chemical looping and OTM studies. For such materials, it would be useful to compare these two approaches and here we perform this by looking at hydrogen production rates relative to the mass of OCM or membrane that is used (a mass basis is logical in that a membrane can always be simply ground into powder form and used as a looping agent if this is likely to be more effective). In particular the group of Zaspalis have published a body of work^{68, 135, 136, 226, 227} in which they use similar perovskite materials as both OCMs and membranes. The group of Metcalfe *et al.* have also used similar perovskites for these two applications^{67, 141}.

Zaspalis's work¹³⁵ can be used to obtain a mass-specific rate of hydrogen production for chemical looping. Comparison with membrane operation is complicated by the fact that, within this paper¹³⁵, different overall reactions are used for the thermogravimetric work, the chemical looping and the membrane studies. $\text{La}_{0.3}\text{Sr}_{0.7}\text{FeO}_3$ was used for chemical looping steam-methane reforming (CLSMR) and for this reaction had a capacity of about $286 \mu\text{mol H}_2 \text{ g}^{-1}$ of hydrogen production through oxidation of the reduced $\text{La}_{0.3}\text{Sr}_{0.7}\text{FeO}_3$ with water. It is not possible from the data to calculate the timescale over which this oxidation took place as the data is plotted versus amount of water injected. The reoxidation in the thermogravimetric experiments is very fast (performed with methane as the reduction gas and oxygen as the oxidant, CLPO) with a slower reduction giving an

overall cycle (neglecting the inert gas exposure) of approximately 50 minutes and therefore a hydrogen production rate of about $6 \mu\text{mol H}_2 \text{ g}^{-1} \text{ min}^{-1}$. It is not possible in this paper to calculate the hydrogen production rate in the membrane system (which was used for membrane-based WGS, carbon monoxide on one side and water on the other) as the inlet gas flow rates and the exit gas composition are not given (only mass spectrometer ion currents versus time are given for the exit gas). However, the authors state the production rate to be $47.5 \text{ cm}^3 \text{ H}_2 \text{ (STP) m}^{-2} \text{ min}^{-1}$ ($0.003 \mu\text{mol cm}^{-2} \text{ s}^{-1}$) for the rate of hydrogen production when carbon monoxide is replaced with inert at 860°C (i.e., a case of no chemical driving force; a rather surprising result). In their later work⁶⁸ with an $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3$ OTM they report a production rate of $187 \text{ cm}^3 \text{ H}_2 \text{ (STP) m}^{-2} \text{ min}^{-1}$ ($0.012 \mu\text{mol cm}^{-2} \text{ s}^{-1}$) or about $8 \times 10^{-3} \text{ mol H}_2 \text{ m}^{-2} \text{ min}^{-1}$. For a 3 mm thick membrane with a bulk density of $ca 6 \text{ g cm}^{-3}$ ²²⁸ this equates to $0.5 \mu\text{mol H}_2 \text{ g}^{-1} \text{ min}^{-1}$. In the case of the 1 mm thick membrane the production rate is three times higher, and the amount of membrane material three times lower, and therefore the mass-specific rate of hydrogen production is about an order of magnitude greater at $4 \mu\text{mol H}_2 \text{ g}^{-1} \text{ min}^{-1}$. This is a very similar value to the rate of hydrogen production from chemical looping albeit for a different material stoichiometry and a different reaction.

The work of Metcalfe *et al.*⁶⁷ indicates a rate of hydrogen production from CLWGS with $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3$ of $0.2 \text{ cm}^3 \text{ (STP) min}^{-1}$ (1% mole fraction of hydrogen is completely converted in a $20 \text{ cm}^3 \text{ (STP) min}^{-1}$ flow) for a 50 mg sample giving $180 \mu\text{mol H}_2 \text{ g}^{-1} \text{ min}^{-1}$ over the oxidation cycle (lasting approximately 10 minutes) or, assuming a reduction cycle similar in length to the oxidation cycle (reasonable from the data presented), $90 \mu\text{mol H}_2 \text{ g}^{-1} \text{ min}^{-1}$ over an entire cycle. Note that $1800 \mu\text{mol H}_2 \text{ g}^{-1}$ removed over 10 minutes is close to the full oxygen capacity of the material (assuming the material can be reduced to $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_{2.5}$ gives a capacity of $2200 \mu\text{mol O g}^{-1}$. At 900°C , their $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ membrane¹⁴¹ gave a production rate of $0.05 \mu\text{mol H}_2 \text{ s}^{-1}$ for a 6 cm^2 membrane area (1.5 mm outer diameter, four microtubes, isothermal length of 3 cm) or $0.5 \mu\text{mol H}_2 \text{ cm}^{-2} \text{ min}^{-1}$ ($5 \times 10^{-3} \text{ mol H}_2 \text{ m}^{-2} \text{ min}^{-1}$). This is a very similar value to the permeation rate seen by Zaspalis for 3 mm thick $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3$ OTMs but here Metcalfe used 250 μm wall-thickness membranes. For a 250 μm thick membrane with a bulk density of $ca 6 \text{ g cm}^{-3}$ ²²⁸ (the perovskites under question here have similar bulk densities) this $0.5 \mu\text{mol H}_2 \text{ cm}^{-2} \text{ min}^{-1}$ equates to $0.075 \mu\text{mol H}_2 \text{ g}^{-1} \text{ min}^{-1}$. This is some three orders of magnitude lower than the rate of hydrogen production from chemical looping (note, however, that this rate may have been limited by the supply of reactant as the water conversion was very high indicating that much higher rates could have been achieved). In terms of area available in the two systems the membrane exhibits $6 \text{ cm}^2 \text{ g}^{-1}$ while the OCM exhibits $6 \text{ m}^2 \text{ g}^{-1}$ and it is possible that the difference in production rates is due to the difference in specific areas. The critical length (the length scale at which there is a transition from bulk diffusion control to surface control of the redox reactions, evaluated by dividing the diffusion coefficient by the surface exchange coefficient) of this material is about $300 \mu\text{m}$ ²²⁹. The powdered materials appear to

employ a significant fraction of the available oxygen capacity. This is a result of the value of the critical length of the material being much less than the crystallite size. A decrease in membrane thickness would not be expected to increase production rate as the membrane would be in a region of surface control but it would increase the mass specific rate. A decrease by a factor of 50 in thickness to a value comparable to the 5 μm crystallite size used in the chemical looping study⁶⁷ would then result in a production rate of 4 $\mu\text{mol H}_2 \text{ g}^{-1} \text{ min}^{-1}$, still much lower than the chemical looping rate of 90 $\mu\text{mol H}_2 \text{ g}^{-1} \text{ min}^{-1}$. However, it should be noted that the surface area of the powders is of course much higher than would be expected for dense 5 μm crystallites.

Clearly the production rate of hydrogen is not the only concern in these systems. The selectivity for hydrogen production (specifically avoiding unwanted side reactions) and the durability of the OCM or membrane is critical. Zaspalis *et al.*¹³⁶ do not comment on selectivity in their systems, however, Metcalfe *et al.*⁶⁷ indicate that the carbon monoxide mole fraction is less than 50 ppm in a stream that produces 1% hydrogen (i.e. the selectivity to unwanted carbon monoxide is less than 0.5%). In the case of the membrane systems there are no problems with selectivity as such, however, there may be leaks across the membrane. Zaspalis¹³⁵ does not mention any leaks, nor does he report the minimum leak that could have been detected. Metcalfe¹⁴¹ quantified membrane leak rates as being as high as one order of magnitude lower than oxygen permeation rates. This would indicate that working membranes could give an effective selectivity to contaminants that would be appreciably higher than the looping systems. In the case of durability Metcalfe *et al.*⁶⁷ operated the chemical looping over about 150 cycles (3,000 minutes using the basis of 20 minute cycles – although the cycles themselves were longer in practice). Zaspalis does not seem to have performed many cycles. Metcalfe reports membrane operation over 400 hours (24,000 minutes); Zaspalis appears to have operated his membranes for much shorter times. However, it would seem reasonable to assume that any material that can survive 24,000 minutes of operation as a membrane should also be able to survive a similar length of time as an OCM. The durability of OCMs may therefore be underestimated; they are not tested to destruction in the way that membranes often are^{xi}. It would appear that, when one takes into account the cost

of membrane fabrication, membrane integrity (leaks) and durability must be excellent if membranes are to compete with chemical looping systems.

5. Commercialisation, challenges and future opportunities

Commercialisation of chemical looping and membrane processes to some extent will be dependent upon successful demonstration at the pilot scale. OTMs for the partial oxidation of, e.g., methane are already close to commercial application following the intensive development work of Air Products and Chemicals and partners and Praxair over the past decade²³⁰. In terms of chemical looping partial oxidation, Mayer *et al.*²³¹ have recently demonstrated pilot scale application using a dual circulating fluidised bed pilot plant operated over 36 hours; 45 kg of a nickel-based OCM were used. It is interesting to note that the membrane-based processes appear to be more advanced than the chemical looping processes (recall that at the end of Section 1 we speculated that chemical looping processes should be more attractive). This success of membrane-based processes may be the result of key industrial players backing one technology and if so commercial opportunities for looping processes exist.

In contrast, there does not appear to have been any pilot scale work involving water-splitting processes such as CLWGS and its membrane analogue. This may in part be as a result of the overall endothermic nature of these processes compared to the exothermic POM reaction. It may be possible for the field of membranes to take some process ideas from the field of chemical looping. One of the most recent developments in chemical looping is the use of a three-stage or three-reactor looping process for hydrogen production which involves two oxidation processes, one in air and one in water. This enables overall autothermal operation. As previously stated, for every looping system there is an analogous membrane system. In this case the equivalent membrane system would involve e.g., tubular membranes with fuel on the shell side and different feeds on the lumen side, some with water and some with air as depicted in Figure 6.

Figure 6. Representation of the autothermal water-splitting concept. Methane is combusted by (a) oxygen separated from air by one set of membranes. The other set of membranes (b) perform water-splitting for high purity hydrogen production.

^{xi} It should be noted that recent work by Kozhevnikov, I. Leonidov, M. Patrakeeve, A. Markov and Y. Blinovskov, *Journal of Solid State Electrochemistry*, 2009, 13, 391-39, and A. Markov, M. Patrakeeve, I. Leonidov and V. Kozhevnikov, *Journal of Solid State Electrochemistry*, 2011, 15, 253-257, has indicated that $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$ membranes, in this case for the partial oxidation of methane, may be stable for more than 7,000 hours and achieve oxygen fluxes of 7 $\text{cm}^3 \text{ cm}^{-2} \text{ min}^{-1}$. Assuming that this flux applies at STP for molecular oxygen this equates to 625 $\mu\text{mol O cm}^{-2} \text{ s}^{-1}$. For a 1 mm membrane with a density of 6 g cm^{-3} this translates to 1000 $\mu\text{mol O g}^{-1} \text{ min}^{-1}$, one order of magnitude higher than chemical looping production rates (note that these looping rates are for the different reaction of steam-methane [Type text])

reforming which involves water-splitting and will undoubtedly suffer from slower kinetics)

The balance between the number of tubes containing water versus air and their flow rates and conversions would determine whether autothermal operation is achieved. Demonstration of such a membrane system is awaited.

Other technical barriers for the commercialisation of water-splitting processes involve ensuring high water utilisation as low water conversion will impose an energy penalty in terms of an increased water/steam recycle and energy for evaporation. Less favourable thermodynamics will also result in reduced driving forces for oxygen transfer. Combined hydrogen and syngas production also of course means that such processes need to be integrated with other processes demanding both of these product streams.

Increased patent activity in the areas of chemical looping²³² (in general and not just hydrogen production) and membrane systems for hydrogen production²³³ reflect increased industrial interest in both areas. To aid further commercial uptake there should be an emphasis on standardisation of experimental protocols, a more sophisticated approach to kinetics to aid design, better microstructural characterisation and innovative new ideas for new membranes and OCMs.

The area would benefit from standardisation of experimental protocols and reporting of data. This could for example include the reporting of (i) membrane history prior to and during operation (ii) duration of operation (iii) quantification of trans-membrane leaks and (iv) simultaneous analysis of both gas streams exiting the membrane reactor to obtain a comprehensive material balance. Occasionally, a material is reported that provides a remarkable oxygen flux which is used in applications such as those reviewed here but problems may arise with reproducibility of the work by other groups. Attention to (i) may prevent such discrepancies in apparent performance and confirm that the new material is worthy of further investigation. However, repeated failure to reproduce the results may indicate that the new material does not warrant further study, saving effort. Furthermore it could be envisaged that, under a standardised experimental protocol, a material that does not operate continuously e.g., for 100 hours cannot be reported in the open literature. However, work published in a number of journals will be subject to different emphasis and requirements making standardisation difficult. A freely accessible data base into which workers in the area can provide a standard set of parameters with respect to the experimental details and reporting of results would be of significant benefit.

In contrast looping is a more mature field and there is already a clear emphasis on durability and cycling. However, the nature of kinetic investigations needs to be improved to include a better understanding of the flow patterns in the reactors employed and operation under conditions appropriate to accurate determination of kinetics (such kinetics allow reactor design to be performed). This normally would mean operation at differential conversions such that the gas phase, and indeed the solid phase, conditions are known and essentially invariant in the reactor. Such careful work needs to be coupled with the use of 'product' gas stream (e.g., pure carbon monoxide should not be used as a

reducing gas alone as this just gives an idea of kinetics at the inlet conditions). Partially converted feeds, i.e., carbon monoxide and carbon dioxide mixtures must also be used. This will probe the kinetics of the processes at different conversions. Different conversions in e.g., a fixed bed looping reactor would allow one to develop an understanding of the kinetics at arbitrary positions in the bed leading to a more robust modelling and design approach. The same criticisms and needs of course also apply to membrane systems.

In addition to the surface processes that must occur, solid state transport processes are important for both membranes and looping materials. Clearly, parameters such as grain boundary density and indeed grain boundary composition (which may in general be different from bulk composition of the material) will be important. There is an awareness that the microstructure of the solid phase may have an important role but there is a lack of work in this area. Indeed if the membrane or looping material transport processes could be adequately described on this microscopic level then, in combination with a kinetic understanding, models of the material could be developed that would be capable of predicting performance both as a membrane and as a looping material. Such an approach would have clear benefits including material microstructural optimisation and may indicate new opportunities in areas such as grain boundary engineering (control of grain boundary density and composition).

A novel approach for looping materials would be to separate the surface and storage properties, that currently one unique material must possess, and rather adopt a hybrid approach. For example consider the iron oxide looping system. Under unfavourable conditions, particularly if unsupported, pellets can fragment and material can be lost. Consider now iron oxide encapsulated within a hollow microsphere. The microsphere possesses oxygen permeability as it is fabricated from a mixed oxygen-ion and electron conductor; it acts as a membrane. The diameter of the sphere allows a thin wall (less than the critical length of the material) to be used resulting in rapid oxygen transfer across the wall. The iron oxide will still fragment but the material will remain contained within its host structure. Such an approach would of course require rather sophisticated methods of fabrication but if the benefits were great enough these could be justified. There are in addition other similar structures that could be envisaged that might be simpler to employ practically.

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