CONFERENCE PROCEEDINGS

Comparison of Ion Transport Membranes

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FOURTH ANNUAL CONFERENCE ON CARBON CAPTURE AND SEQUESTRATION DOE/NETL
May 2-5, 2005

Abstract

One promising Zero Emissions Power Plant approach requires fuel to be combusted in a mixture of oxygen and carbon dioxide, to aid the later capture and sequestration of carbon dioxide. However current methods of oxygen production are energy intensive and so reduce the efficiency and power output of the plant. A relatively new technology, which can solve this problem, involves Ion Transport Membranes (ITMs), which are permeable to oxygen and no other substance and require significantly less energy per unit of oxygen than current methods of oxygen production.

Much research has been conducted on ITMs, both as oxygen producers and when used to partially oxidate methane for syngas production. However, these studies have been conducted at different temperatures and oxygen partial pressures, using membranes with different thicknesses and surface geometries. All of these factors affect the oxygen flux through the membrane. The aim of this paper is to compare the many different membrane materials in a manner that takes account of the effects of these experimental parameters.

1. Introduction

1.1 Zero Emissions Power Plants

Zero Emissions Power Plants (ZEPPs) are power plants with absolutely no emissions. This is achieved by capturing the products of combustion, including carbon dioxide, condensing out the water and compressing them to liquid form. The easiest way of doing this is to burn the fuel in a mixture of carbon dioxide and oxygen, instead of in air. The only products of combustion are carbon dioxide and steam, which drive a gas turbine. They are then easily separated by condensing out the water. The hot water can then be used for heating in buildings near to the power station. Some of the carbon dioxide is recirculated to be mixed with oxygen and returned to the combustion chamber. The rest is compressed to liquid, which can then be sold to industry or sequestered. No emissions of any kind are released. The oxygen required for combustion must be separated from the air, however mature oxygen production technologies are energy intensive and so the overall efficiency of the power plant is reduced.

1.2 Ion Transport Membranes

Ion Transport Membranes (ITMs) are ceramic membranes that are permeable to oxygen and nothing else. Much research has been conducted into the use of ITMs to oxygenate a sweep gas. There has also been a substantial amount of research on ITMs used to convert methane to syngas, a reaction that consumes oxygen. Wang *et al.* (2003) found that the flux across a tubular membrane when used in this way can be up to 8 times the oxygen flux when used to oxygenate a sweep gas. Most ion transport membrane materials are only permeable to oxygen at temperatures above 700°C (975 K). The membrane therefore needs to be heated, however the energy required is significantly less than for other forms of oxygen production.

There are three main types of ceramics with ion transport capabilities: perovskite, fluorite and mixed. Perovskite ion transport ceramics have the chemical structure ABO_3. There may be a mixture of 2 or more elements in the A-site and / or the B-site, e.g. $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$. Fluorite ion transport ceramics have the structure AO_2, e.g. ZrO_2. Both types can conduct both electrons and oxygen ions through the ceramic lattice. Most materials are better at conducting either electrons or oxygen ions. Also, some membranes may have very high ionic conductivity but low stability in a particular environment. Mixed membranes are simply membranes made of a mixture of two materials, in order to take advantage of the best traits of each.

New materials are being created constantly, and there are many reports available on the properties of various oxygen ion transport membrane materials, as a number of different groups and individuals around the world are conducting research into this area. However, the experimental research has been conducted at different temperatures, pressures, oxygen concentrations, and membrane geometries. This paper aims to provide a comparison of the newest materials (2000 – 2004) in a manner that takes into account these

differences. The useful property of these membranes is the oxygen flux, i.e. the amount of oxygen passing though 1 cm^2 of the membrane per unit time. Perovskite are the materials that have attracted most research in resent years, as they have higher fluxes in the 700°C – 1000°C range than fluorite membranes do.

1.3 Applications of Ion Transport Membranes

Zero Emissions Ion Transport Membrane Oxygen Power (ZEITMOP) is one possible ZEPP cycle, introduced by Yantovski *et al*. (2003). It uses ITMs to separate oxygen from air and mix it with carbon dioxide. Fuel is then burned in this mixture, and the water is condensed out. Some carbon dioxide is captured for sequestration, with the rest returned to the ITMs for reoxygenation. This method of oxygen production requires significantly less energy per unit oxygen than other processes. This increases the efficiency of the zero emissions power plant. AZEP is another possible ZEPP cycle, currently being developed by the Griffin *et al.* (2003, 2004). This cycle also uses ITMs to oxygenate flue gases returning to the combustion chamber.

Like power plants, internal combustion engines burn a fuel to create energy and combustion products. The ZEMPES (Zero Emissions Membrane Piston Engine System) cycle, created and developed by Yantovski *et al*. (2003, 2004, 2005) burns fuel in carbon dioxide and oxygen, and the combustion products, carbon dioxide and water vapour, are separated and reoxygenated using ITMs in a similar manner to a ZEPP.

When there is a higher oxygen partial pressure on one side of a membrane than the other, oxygen will pass through from the oxygen-rich side to the oxygen-lean side. ITMs can therefore be used to create oxygen in many other applications unrelated to syngas. In testing the oxygen flux under these conditions, a sweep gas is used on the permeate side, and an oxygen-containing gas, normally air, is used on the feed side. The flux is then measured by analysing the oxygen concentration at the exit of the permeate side.

Methane is more abundant than oil; however a number of methane fields are in remote locations. The methane would be more useful if it were to be converted to liquid. An important step in this process is the catalytic partial oxidation of methane to synthesis gas, or syngas. Syngas is a mixture of carbon monoxide and hydrogen, and is formed by a reaction between oxygen and methane in the presence of a catalyst. ITM tubes can be packed with this catalyst (or a plate can be coated with it). If methane flows on the catalyst-containing side, the oxygen that passes through will be quickly used up in the reaction. This causes a continually low oxygen pressure on the permeate side, and so greatly increases the oxygen flux.

2. Theory

There are a number of factors that affect the passing of oxygen through the membrane. Firstly the oxygen must reach the membrane. It is possible that due to transport in the flow of gas on the feed side of the membrane the flux could be limited. Wang *et al.* (2002) found that the oxygen flux increased with feed side flow rate up to a flow rate of 150 mL/min for one set of experiments. Below this value less oxygen was reaching the membrane than could pass though, i.e. transport to the surface was a limiting factor. Therefore all values used in this paper from those experimental results are taken at feed side flow rates of more than 150 mL/min.

After the oxygen reaches the membrane it is adsorbed onto the surface. Surface exchange effects can be identified by a difference in the normalised values for different thicknesses of the same material. Diethelm *et al*. (2003) normalised the flux through $La_{0.4}Ca_{0.6}Fe_{0.75}Co_{0.25}O_{3-\delta}$ membranes of different thicknesses to a thickness of 1 mm. As the results were at the same temperature and similar partial pressure differences, it was expected to have almost identical results, yet higher normalised results were found for a membrane 1.745 mm thick than one 0.716 mm thick. This implies that surface exchange effects were slowing down the oxygen transport, i.e. oxygen could travel through the bulk of the material faster than it could be adsorbed onto the surface. This limit did not reduce the flux through the thicker material to the same extent as the thinner, as there was less travelling through the thicker sample in any case. This was obvious as the normalised flux through the thinner membrane is lower than the normalised flux through the thicker.

Once the oxygen has reached the surface and been adsorbed onto it, it is transported through the ceramic by bulk transport through the ceramic lattice, which contains oxygen ion vacancies. When

heated, excited oxygen ions can travel through the lattice using these vacancies. The oxygen flux across the membrane is given by the Nernst-Einstein equation:

$$j_{O_2} = \frac{\sigma_i RT}{4Ln^2F^2} \ln\left(\frac{P_1}{P_2}\right) \quad (1)$$

where j_{O_2} is the oxygen flux through unit area, σ_i is the material's ionic conductivity, R is the ideal gas constant, T is the absolute Temperature, L is the membrane thickness, n is the charge on the charge carrier, which is always 2 for oxygen ions, F is Faraday's constant, P_1 is the oxygen partial pressure at the feed side, and P_2 is the oxygen partial pressure at the permeate side.

Above 700°C (975 K) the flux is directly proportional to the absolute temperature and inversely proportional to the thickness of the membrane. The flux is also proportional to the natural log of the ratio of oxygen partial pressures across the membrane. This explains why the flux can be much higher when an oxygen-consuming reaction occurs on one side of the membrane.

3. Comparing the different membrane materials

3.1 Materials to be compared

New ITM materials are continually being created and tested. The results of tests on the following materials have been published in the period 2000 – 2004. This paper is a comparison of these materials.

Name	Formula	Author	Year
BBCF	$BaBi_{0.4}Co_{0.2}Fe_{0.4}O_{3-d}$	Shao *et al.*	2000
BCF	$BaCe_{0.15}Fe_{0.85}O_{3-d}$	Zhu *et al.*	2004
BSCF	$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-d}$	Wang, *et al.*	2002
BTCF	$BaTi_{0.2}Co_{0.5}Fe_{0.3}O_{3-d}$	Tong *et al.*	2003
CLFC	$Ca_{0.6}\ La_{0.4}Fe_{0.75}Co_{0.25}O_{3-d}$	Diethelm, *et al.*	2003
LCF	$La_{0.4}Ca_{0.6}FeO_{3-d}$	Diethelm, *et al.*	2003
LCFC	$La_{0.6}Ca_{0.4}Fe_{0.75}Co_{0.25}O_{3-d}$	Diethelm, *et al.*	2004
LSC	$La_{0.5}Sr_{0.5}CoO_{3-d}$	Van der Haar	2001
LSCF	$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-d}$	Shao	2003
LSGF	$La_{0.15}Sr_{0.85}Ga_{0.3}Fe_{0.7}O_{3-d}$	Shao	2003
LSGF-BSCF	$12.8La_{0.15}Sr_{0.85}Ga_{0.3}Fe_{0.7}O_{3-d}$ $Ba_{0.5}Sr_{0.5}Fe_{0.2}Co_{0.8}Fe_{0.2}O_{3-d}$	Wang *et al.*	2003

The tests were carried out at different temperatures and oxygen partial pressures, using different units, membrane thicknesses and geometries. As a result, it was necessary to normalise the results to standard values.

3.1 Normalising the results

Oxygen flux is measured in different units. Some results are given in mL/(cm^2 min), others in µmol/(cm^2 s). It was assumed that mL/(cm^2 min) was at Standard Temperature and Pressure. The ideal gas law was used to convert these results to µmol/(cm^2 s). Wang *et al.* presented results in both mL/(cm^2 min), and µmol/(cm^2 s). It was found that the values converted to µmol/(cm^2 s) using the ideal gas/STP assumption agreed with the reported µmol/(cm^2 s) values to within ± 5% accuracy, or to within +/- 0.1 µmol/(cm^2 s), confirming that the ideal gas / STP assumption was reasonably correct.

This paper normalises all the results to 875 °C (= 1148 K). Most reports include 875°C in the results; this was one of the reasons this was chosen as the normalised temperature. Graphs of flux as a function of temperature are also shown. In theory the relationship between the flux and temperature is linear, and in the literature this is shown to be reasonably true in practice. Therefore linear interpolation, or simply reading the desired value off a line drawn on a graph, is acceptable in cases where there is no value reported at 875°C.

This paper normalises all the results to 1 mm membrane thickness. Flux is, in theory, inversely proportional to the thickness of the membrane, so multiplying by the thickness in mm should normalise to 1 mm thickness. If surface exchange is limiting the flux, this can cause normalised results to differ for samples of the same material, with different physical thicknesses. In cases where information was available for samples of thicknesses greater and lesser than 1 mm, interpolation was used to estimate the flux at a physical thickness of 1 mm.

The flux is proportional to $\ln(P_1/P_2)$. However, in experiments it is easy to maintain P_1 constant, but very hard to ensure P_2 is constant along the membrane. Values for P_1 were available for all the materials, but values for P_2 were not, so normalising to a particular partial pressure ratio proved impossible. However, there is a relationship between P_1 and flux, albeit not a linear one. In the absence of information on P_2, it was decided to normalise the results to P_1 = 0.21 atm instead of normalising to a particular partial pressure ratio. This value was chosen as it is the atmospheric oxygen partial pressure. Most experiments provided results for this partial pressure.

3.2 Oxygen production mode

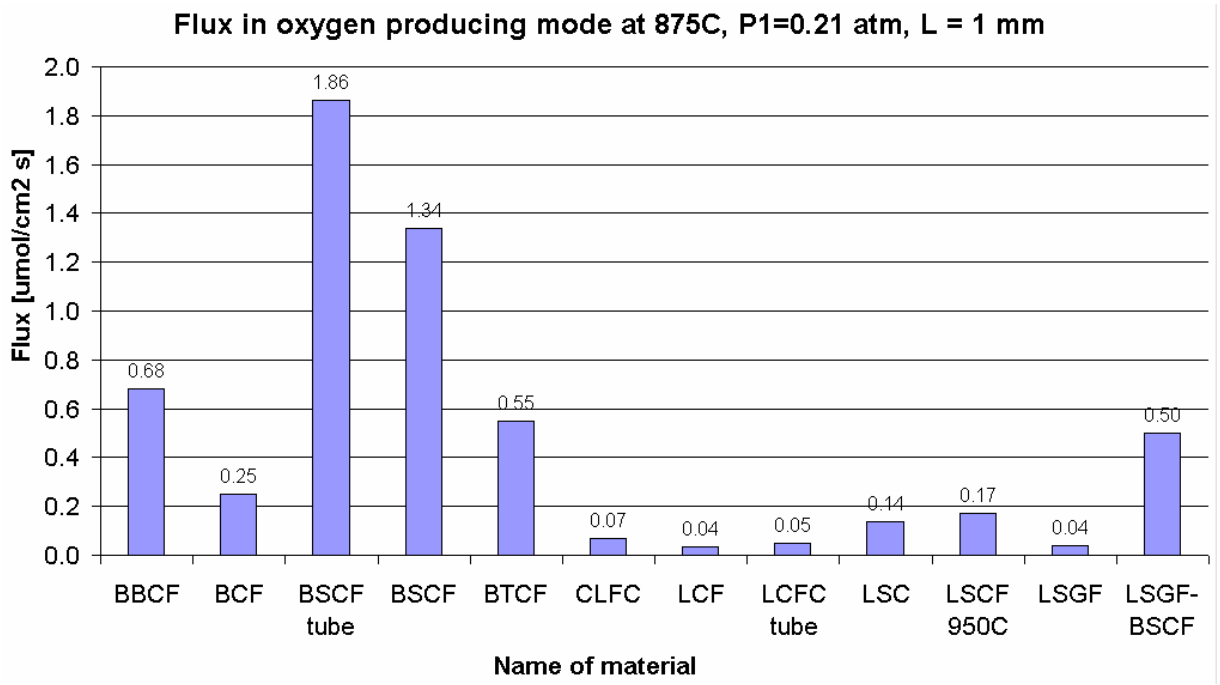

Fig. 1 Flux in oxygen permeation mode for the various materials

It appears BSCF, or $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ has the highest flux in oxygen permeation mode, and is therefore the "best" material in this application. Geometries are discs unless otherwise stated.

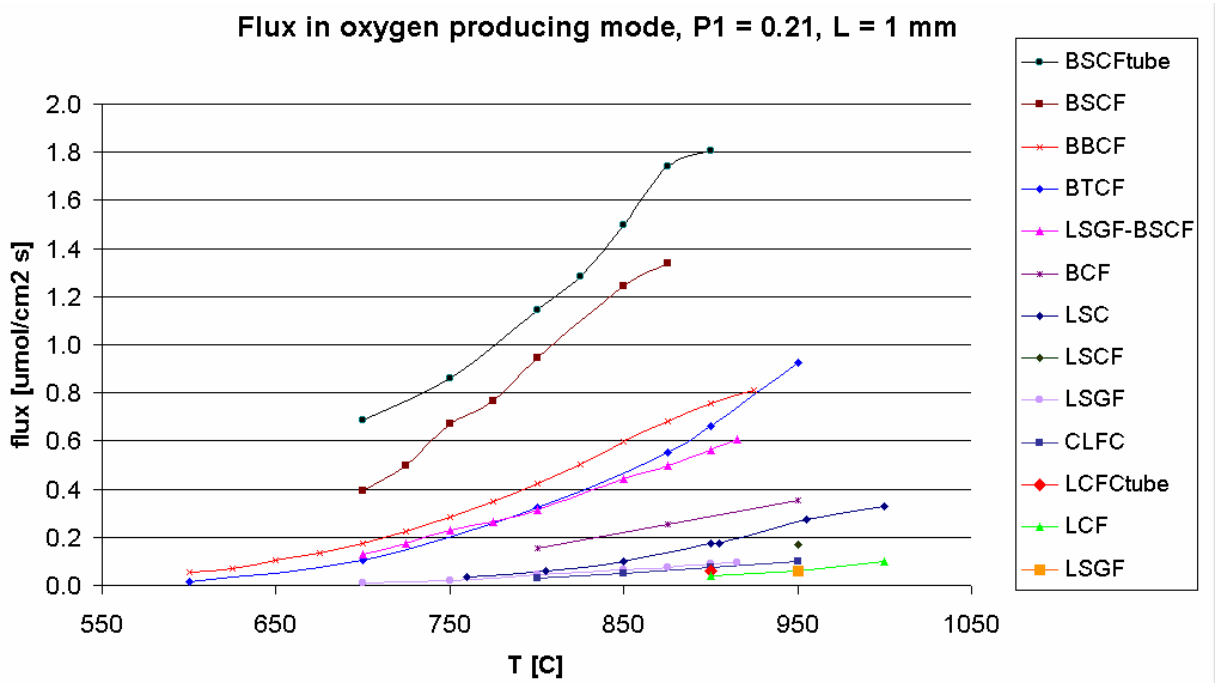

Fig. 2 Flux in oxygen permeation mode with respect to Temperature for the ITM materials. The names are listed in order of decreasing flux.

Again, it is clear to see that BSCF is the best material. Most materials' fluxes have a linear relationship with Temperature.

3.3 Stability in a hydrogen-containing atmosphere

Syngas consists of CO and H_2. It was assumed that any membrane used to convert methane to syngas would need to be stable in an environment containing hydrogen. The following materials have been tested in such an environment:

BSCF	Structure destroyed, recovered by oxidation
BTCF	Structure destroyed, recovered after ½ hour in 1% Oxygen
BCF	Maintains structure at 900°C in hydrogen containing environment
CLFC	Flux measured in hydrogen environment, degraded from 0.8 µmol/cm^{2}s to 0.6 µmol/cm^{2}s Remained constant at 0.6, even after thermal cycle
LCF	After 600 hours, surface exposed to H_2 decomposed but bulk unchanged and flux stable
LCFC	Stable in syngas production for 10 days, though some demixing occurred
LSGF	Used to produce syngas for more than a year with no degradation
LSGF-BSCF	Maintains structure at 900°C in hydrogen containing environment
SCF	Structure destroyed, 99.4% recovered after 16 hours in 1% Oxygen

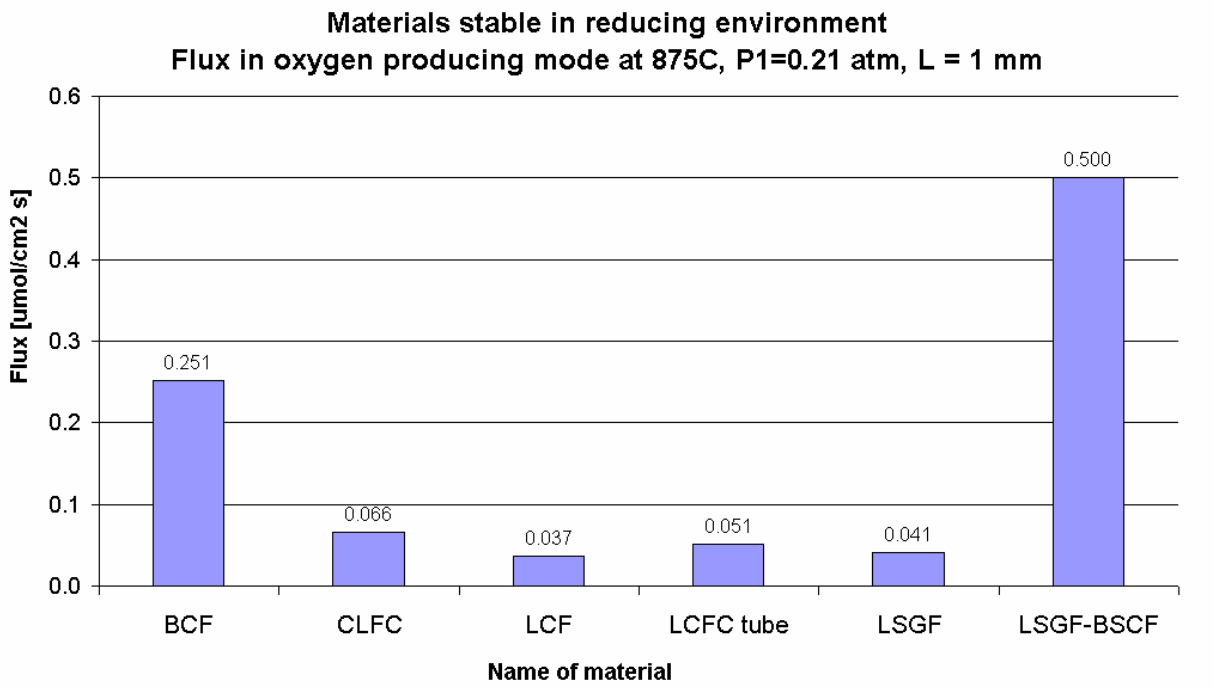

Fig. 3 Normalised flux of materials that are stable in a hydrogen-containing environment

It appears that the mixed membrane material LSGF-BSCF has the highest flux of all the stable materials. This material was created with the aim of using the high flux of BSCF and the high stability of LSCF.

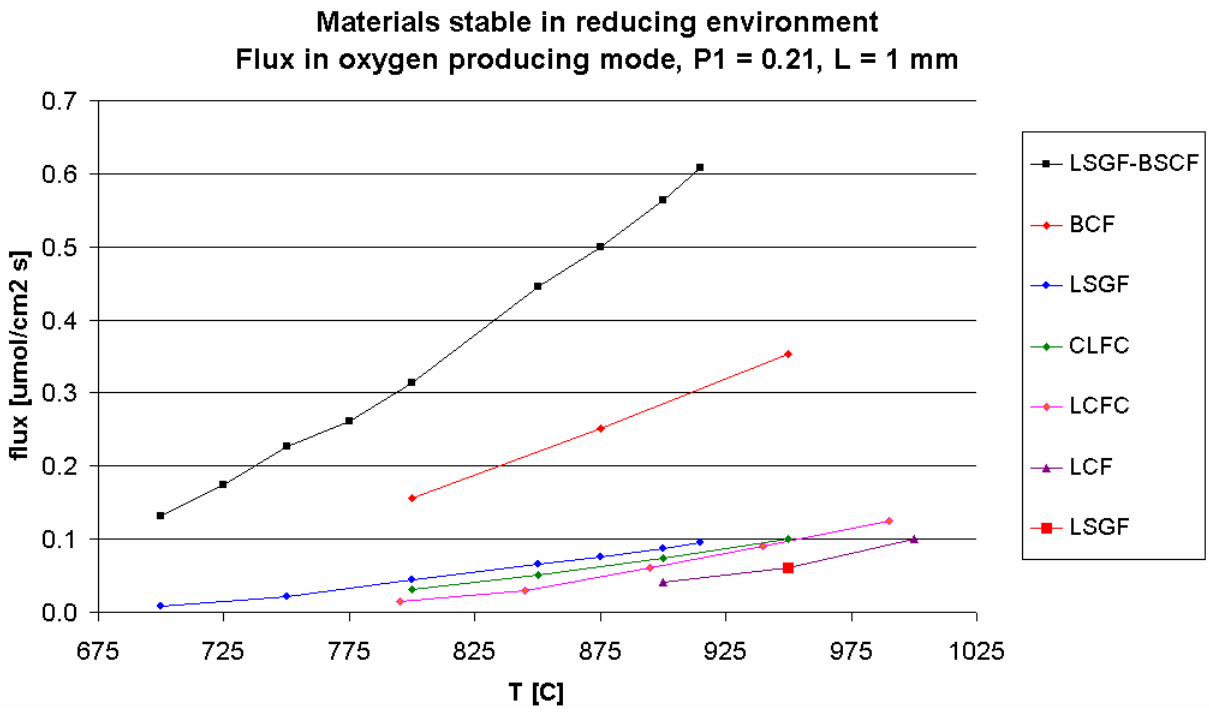

Fig. 4 Flux with respect to temperature for stable ITM materials. The names are listed in order of decreasing flux.

3.4 Syngas production

Values were only provided for oxygen flux in syngas producing mode for two of the new materials.

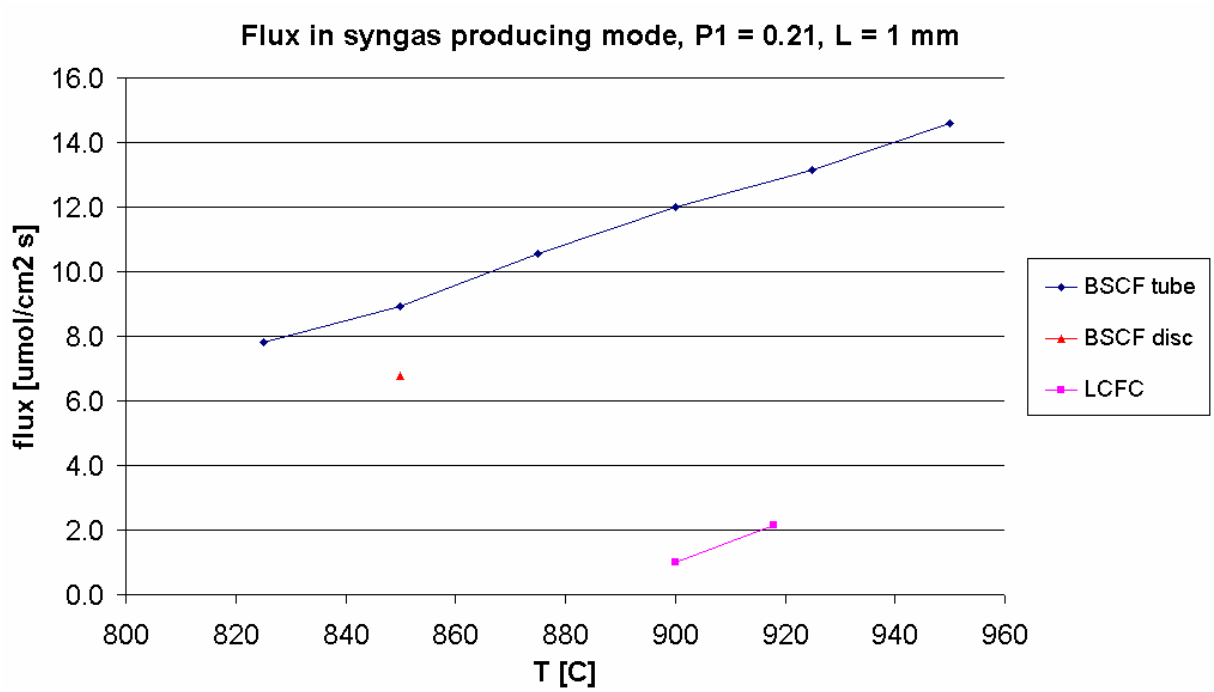

Fig. 5 Flux in syngas producing mode. The names are listed in order of decreasing flux.

Again BSCF is the material with the highest flux. This is surprising, as BSCF is unstable in a hydrogen-containing environment, and it was not only successfully used to produce syngas, but remained stable for 500 hours! Wang *et al.* (2003) examined the catalyst and discovered that the reaction had followed the combustion and reforming mechanism of syngas formation. The methane reacted with the oxygen at the membrane surface, forming carbon dioxide and water vapour, which then reacted with the methane in the centre of the tube. No hydrogen reached the membrane surface, so the membrane was not actually in a reducing environment. There is another mechanism by which syngas may be formed, the direct partial oxidation mechanism. This would allow hydrogen in contact with the membrane surface.

Combustion and Reforming:

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$
$$CH_4 + CO_2 = 2CO + 2H_2 \quad (2)$$
$$2CH_4 + 2H_2O = 2CO + 6H_2$$

Direct Partial Oxidation:

$$4CH_4 + 2O_2 = 4CO + 8H_2 \quad (3)$$

Wang *et al.* (2003) state that at low space velocity ($<10^5$ L/kg h), the reaction would follow the combustion and reforming mechanism, while above this value, it would follow the direct partial oxidation mechanism. So a membrane that is unstable in a hydrogen environment can successfully be used as a syngas reactor if the space velocity is below this value. Above this value a membrane that is stable in a reducing environment is required.

3.4 Thickness

All the results seem to point to BSCF as the membrane material of choice. However, it is not commercially available and has not been developed in a tube less than 1.7 mm thick. LSGF-BSCF has only been created in a disc 1.99 mm thick. LCFC, however, is commercially available in a tube only 0.2 mm thick.

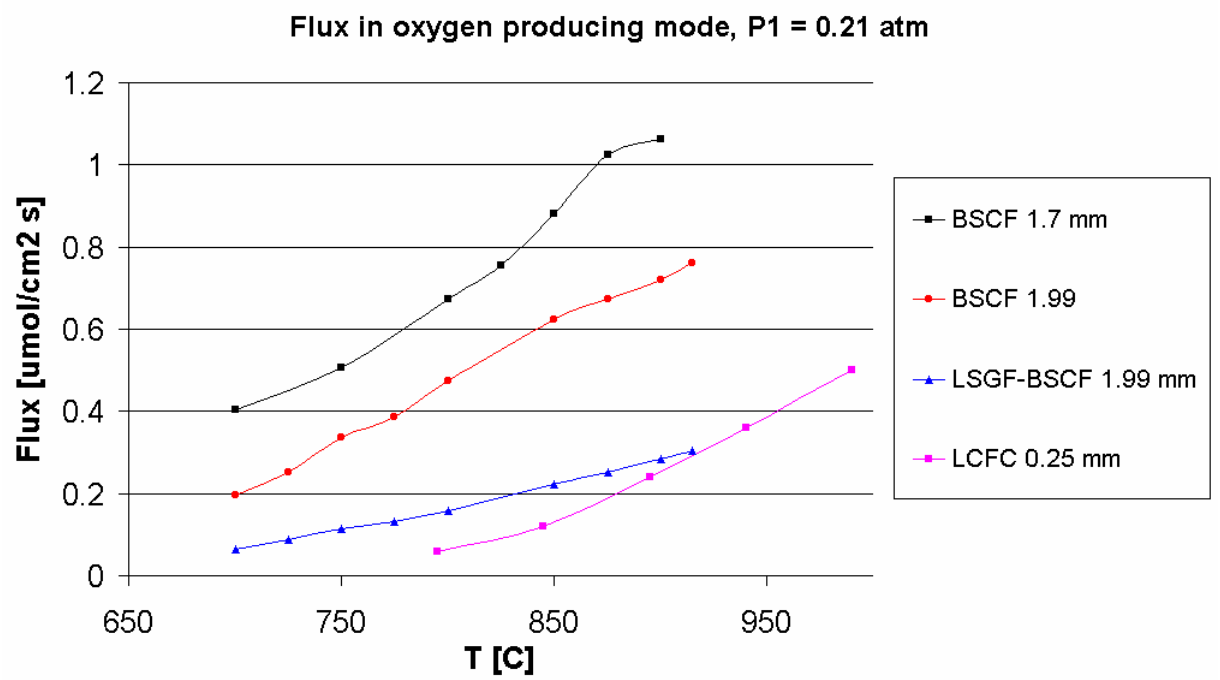

Fig. 6 Actual non-normalised fluxes for membranes with different physical thicknesses. The names are listed in order of decreasing flux.

This figure proves that BSCF really does have an exceptionally high flux. Even the 2 mm thick BSCF membrane surpasses the 0.25 mm thick LCFC membrane. However, thin LCFC tubes may overtake thick LSGF-BSCF discs at very high temperatures, so it is also obvious that reducing the thickness did have a big effect on the flux. A thinner membrane has a higher flux, but it may be physically weaker. Van der Haar (2001) created supported thin-film membranes – a dense membrane supported on a porous substrate of the same material. Using pulsed laser deposition, membranes only 7.5 µm thick were created.

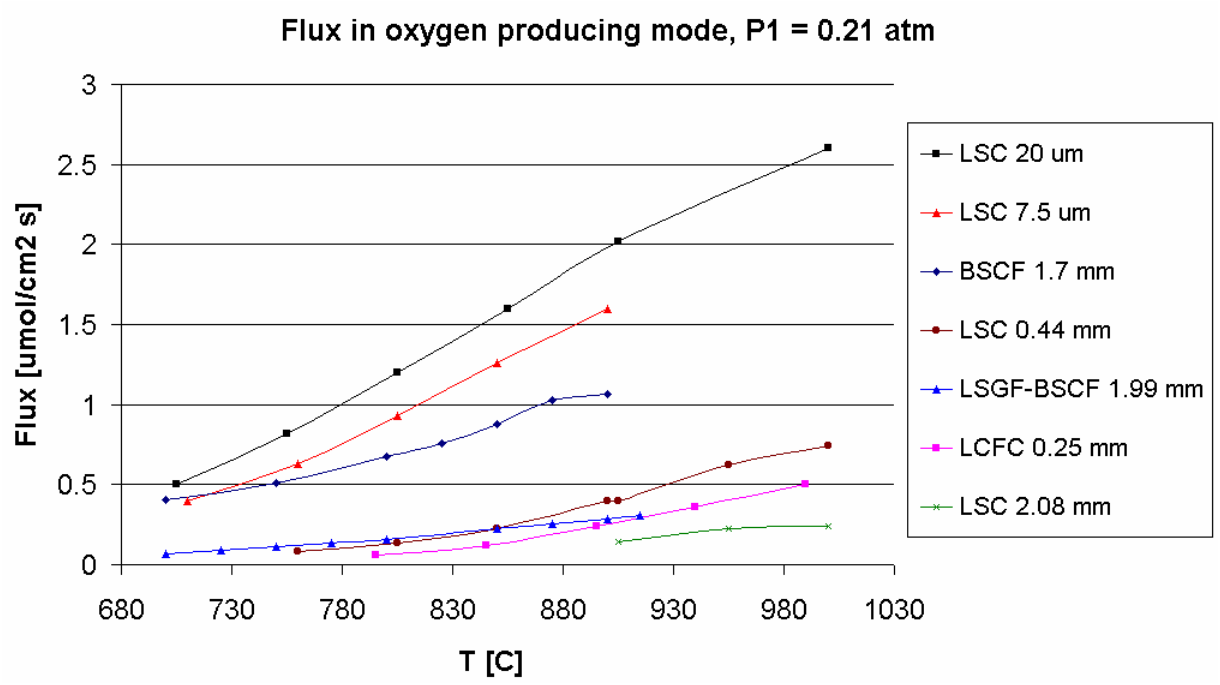

Fig. 7 Flux through membranes of different thicknesses. The names are listed in order of decreasing flux.

The supported thin-film membranes have fluxes much higher than the other membranes. The material, $La_{0.5}Sr_{0.5}CoO_{3-\delta}$, has an unremarkable level of flux when normalised to 1 mm thick. Supported thin-film membranes made of this material can surpass even the BSCF membrane. The flux for the 20 µm thick membrane is actually higher than the flux for the 7.5 µm thick membrane. This implies that, at the micrometer level, thickness no longer affects flux.

4. Conclusions

- BSCF, or $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ appears to be the material with the highest flux among the materials investigated,
- LSGF-BSCF, or $12.8La_{0.15}Sr_{0.85}Ga_{0.3}Fe_{0.7}O_{3-\delta}$ - $1Ba_{0.5}Sr_{0.5}Fe_{0.2}Co_{0.8}Fe_{0.2}O_{3-\delta}$ appears to have the highest flux among materials that are stable in a reducing environment.
- BSCF can be used to convert methane to syngas if it can be ensured that the reaction will follow the combustion and reforming mechanism.
- Supported thin film membranes allow membranes only a few micrometres thick to be created, with very high fluxes.
- At the micrometer level, thickness no longer affects flux.

Acknowledgements

The authors wish to acknowledge the support of the Irish Research Council through the Embark Initiative.

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