Oxygen permeability of cubic yttria-stabilized zirconia at high temperature*

Internal Note - Creative Services sarl

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***Abstract* — A test bench has been developed to study the oxygen permeability of ceramic filters at temperatures up to and exceeding 2200°C. Filters made of yttria-stabilized zirconia, gadolinia-ceria , and mixes of these materials have been tested using oxygen and steam feed gas. Thermal stability could be studied and oxygen permeability data could be obtained.**

***Index Terms* — high-temperature, oxygen permeability, fluorite ceramics, cubic zirconia**

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I. INTRODUCTION

At the end of the last millennium, Prof. Abraham Kogan of the Weizmann Institute in Israel published a series of four articles [1] reporting the results of his experiments to make hydrogen from direct thermal water splitting using concentrated solar power. The last of the four articles reveals the core problem of his experiments: making performing gas filters for high-temperature steam environment. Prof. Kogan attempted some ceramics developments but in the end he gave up.

In direct thermal water splitting (or thermolysis of water) the H_2O molecules are heated to very high temperatures above 2000°C at which they split (or dissociate) in considerable quantity. Heating water and then steam to such temperatures is not so much of a problem. The challenge is finding a filter which can take, at that moment, at least one of the gases out of the dissociated steam.

No filters for extracting hydrogen from steam at these temperatures exist, and we have not been able to identify any material that potentially could be used to make such filters. On the other hand, various refractory oxides with high melting point exhibit oxygen permeability which, when extrapolated to high temperatures, look like promising candidates for making oxygen filters. Unfortunately, quantitative knowledge of oxygen permeability is limited to few materials and ends at about 1600°C.

Our challenge was to develop a test bench for examining the oxygen permeability of filters at highest temperatures and then study filters made from various materials.

* Part of this work has been performed under a development contract with H2 Power System Ltd. at Dublin in the years 2010 to 2013. Klaus Röhrich (klaus@creative-services.fr) and Harald Wirth (herald@creative-services.fr) are researchers at CREATIVE SERVICES, Saint Genis-Pouilly, France.

II. Description of the Experiment

Together with Fraunhofer IKTS at Hermsdorf [1] and HTM Reetz GmbH at Berlin [2], a test bench for examining the oxygen permeability of one-end-closed tubular ceramic filters at temperatures up to and exceeding 2200°C was conceived, designed and constructed.

Fig. 1 The oxygen filter test bench. The components are contained in a steel vessel.

The Testbench is basically a vertical tubular high temperature furnace. Heating elements and thermal insulation are made of graphite and are operated in a protective argon atmosphere. The set-up was tested, without ceramics however, to over 2400°C. The temperature distribution (Fig. 2) is almost flat over a length of about 8 cm. Temperatures are controlled using thermo-elements at different places inside the furnace. The central temperature was measured using a bichromatic pyrometer for which a narrow view channel was cut from the top through the insulation.

The temperature measurement with the pyrometer was not evident due to changes in the reflectivity of the surface that was viewed, due to "fog" from outgassing of heated parts of the furnace and due to solid deposits (dust) in the view channel or on the view window. Eventually thermo-elements and furnace power were calibrated to provide redundancy for the temperature measurements with the pyrometer. We estimate the temperature measurement error at the highest temperatures to less than ±10K.

Through the furnace runs a protective ceramic tube (Fig. 3) separating the graphite heating system in argon atmosphere from the hostile oxygen or steam atmosphere in which the filters are operated. The protective tube is inserted from the bottom. Its inside diameter is 4 cm. It is closed at the top which reaches through and a little beyond the central zone of homogenous heating. At the bottom it is held and sealed by a flange system with arrangements for holding a filter tube, extracting permeate gas, and a feed gas inlet tube (Fig. 4).

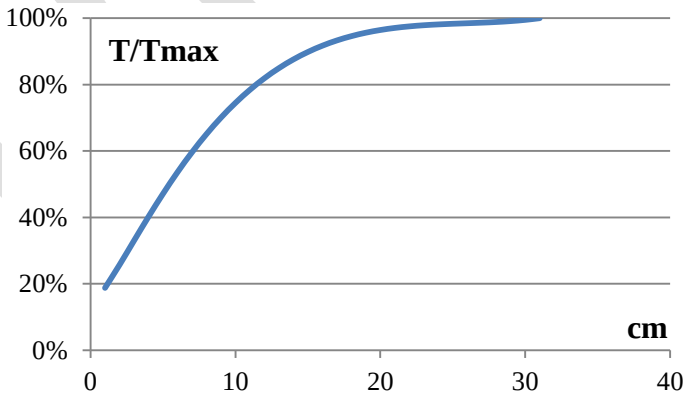

Fig. 2 Temperature profile along the central axis of the cylindrical test bench, inside the protective tube. The profile was determined using thermo–elements at several temperatures between 1200°C and 1800°C and was found to scale. The inside of the protective tube extends from the bottom flange at 0 cm up to about 32 cm (top).

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The protective tube was segmented to avoid cracking under thermal stress. The segment (c. 14 cm long) with the closed end in the high temperature region was made from yttrium-oxide. The other parts were made from aluminium-oxide[3]. We have used the yttrium-oxide protective tube up to about 2280°C[4].

Fig. 3 A protective tube with four segments after use in the test bench.

Fig. 4 An oxygen filter (left, slightly deformed after a test series) as mounted in the set-up. The protective tube was removed but for the lowest segment. To the right of the filter is an inlet tube for the feed gas.

The filters were custom made by Fraunhofer IKTS. The filter tubes were one end closed and typically had an inner diameter of 8 mm with a wall thickness of 1 mm. The filters were mounted inside the protective tube together with an inlet tube for the feed gas. The filters were positioned with their closed end in the middle of the flat T region.

The tests were done at Fraunhofer IKTS. Typically they ran over one day, preheating the furnace in the night before and letting it cool down in the night after the test. Gas was extracted from the filter using a vacuum pump. Feed and permeate gas were measured with flow meters at positions where the gases' temperature was ambient. Data were collected at different temperatures and with different feed gas mixtures using argon, oxygen and steam at atmospheric pressure. The feed gas flow rate was limited by the setup of pumps and meters to the range between 1 ml/min to 100 ml/min for oxygen/argon, and between 250 ml/min and 1250 ml/min for steam.

From the measured flows and pressures the oxygen permeability Q was obtained assuming bulk diffusion (oxygen vacancies diffusion limited transport mechanism):

$$Q = \frac{J \cdot d}{A} / ln\left(P_{feed} / P_{permeate}\right)$$

J oxygen flow [m^3/s]
d wall thickness of filter tube [m]
A filtering surface [m]
P feed and permeate oxygen partial pressure [Pa]

The conductivity σ is the then just a transformation:

$$\sigma = \frac{Q}{T} \cdot \frac{(zF)^2}{R}$$

Q permeability [$m^3/m/s$]
T temperature [K]
z charge number (=4) for O_2 transport ($2xO^{2-}$)
F Faraday constant
R Gas constant

[3] In the course of the development of a protective tube we have experimented with zirconia, hafnia-zirconia and yttria tubes from various suppliers. Hafnia is expensive and zirconia exhibits oxygen permeability. After trials with varying grains sizes and production methods the yttria tubes were slip-cast by Porzellanfarbik Hermsdorf GmbH, pre-cut by Fraunhofer IKTS, both at Hermsdorf, Germany, and finished by Stecher Ceramicparts at Uetendorf, Switzerland.
[4] We observed two problems which lead to the destruction of the protective tubes. The first was reduction on the outside due to the argon atmosphere needed to protect the graphite heating elements. The second was the segmentation which allowed some feed gas –oxygen or steam- to exchange with the furnace argon, react with the graphite and thus act as a vector for carbon to reach the oxide ceramic parts which consequently got, faster or slower, destroyed.

For economically viable hydrogen production from water splitting, oxygen filters with good permeability are needed. Such filters should provide a specific flow of 10 Nml $O_2/cm^2/min$ or more under operating conditions. For concentrated solar powered direct thermal water splitting the typical environment is steam at atmospheric pressure and at temperatures above 2200°C. For mixed electron-ion-conducting materials oxygen transport may be expressed as a conductivity σ. For the case here, σ_{O2} = 200 S/m is the benchmark. With this performance, one square meter of filter surface would extract eight kilograms of oxygen per hour from hot steam leaving one kilogram of hydrogen behind.

For the analysis, the feed gas distribution, composition and dilution (due to extraction) was assumed to be homogenous over the active, i.e. hot, filter surface. This approximation is not always good as explained further below.

The measured permeate gas pressure was corrected for flow resistance and temperature along the pumping line to obtain the oxygen pressure inside the filter. For example a permeate oxygen flux of 26 ml/min at a measured pressure of about 22 Pa, the permeate pressure inside the filter was estimated, at 2150°C, to be 425 Pa. This correction was rather important and great effort was spent detailing the temperature and geometry of the oxygen extraction line.

Also, the measured temperature profile along the filter was used to determine a weighted filter surface. This latter correction was comparatively small, below 5%.

III. Ceramic Oxygen Filters

Various refractory oxides exhibit oxygen permeability which, when extrapolated to high temperatures, look like promising candidates for making oxygen filters for direct thermal water splitting.

To identify potentially interesting filter materials, firstly the materials had to be available, and their processing into filter tubes had to be possible. We excluded radioactive materials like thorium-oxide from the list. Furthermore requirements for the thermal (high temperature) and chemical stability (steam) were applied. The oxygen permeability was anticipated from electron and ion mobility, and related material characteristics.

Our literature sturvey revealed that quantitative knowledge of oxygen permeability at high temperature, say larger than 1000°C, is limited to few materials only and ends at about 1600°C. The figure (Fig. 5) below summarizes our findings for the two most studied materials, stabilized cubic zirconia oxide and cubic ceria oxide, both doped for improved stability or permeability.

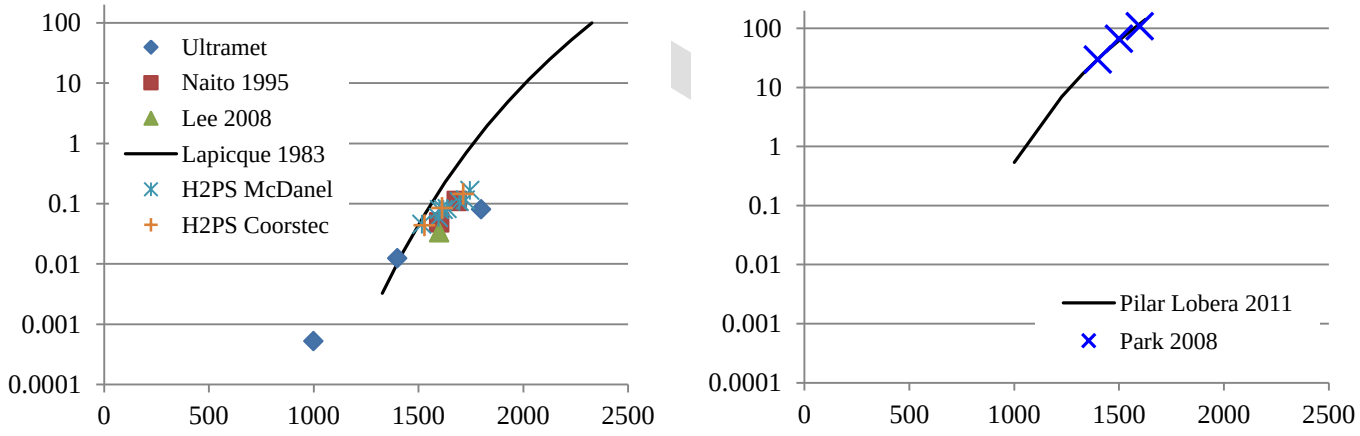

Fig. 5 Published oxygen permeability data plotted as conductivity [S/m] as a function of the temperature [°C].
Left: doped zirconia, refs [4] to [8]; right: doped ceria refs [9] and [10].

For our experiments we used tubular filters with a wall thickness of 1 mm and a diameter of 10 mm. The filters were produced from raw powders by Fraunhofer IKTS in an extrusion process in cooperation with the authors.

We used 8% yttrium stabilized zirconia ("YSZ") for most of the measurements. We had also made and tested filters with 2% co-doped YSZ. The co-dopants were Eu_2O_3, CeO_2, Fe_2O_3 and TiO_2. Within our measurement errors, these co-doped YSZ filters

behave very similar to non doped YSZ filters in steam as well as in oxygen atmosphere.

As a second choice we had made and tested gadolinium doped cerium oxide filters ("CGO" or "GDC"). The very high oxygen permeability however came with reduced thermal strength. These filters got soft and collapsed above 2000°C.

Consequently we tried a mix of the two materials, cubic stabilized ceria-zirconia.

IV. FINDINGS

Our test bench was installed in the laboratory of Fraunhofer IKTS at Hermsdorf where the tests were performed.

For the initial heating we respected a heating rate of typically 5K/sec, however sometimes exceeding 10K/sec. This was done overnight. During operation, after small changes of the parameters, the thermal stabilization of the system took several minutes. A series of measurements typically took between one and two hours. The longest exposure of a filter to oxygen or steam above 2200°C was less than three hours.

We report here results for cubic oxide filters made in three compositions:

"YSZ"	8% Y_2O_3 + 92% ZrO_2
"CGO20"	80% CeO_2 + 20% Gd_2O_3
"Ce-YSZ"	8% Y_2O_3 + 92% (20% CeO_2 + 80% ZrO_2)

Our measurements were limited by several phenomena which we were not able to quantify sufficiently to correct the data. All these corrections would make the permeabilities larger; consequently our results should be considered lower boundaries rather than proper values, in particular when the permeability is high.

A. Cubic Zirconia

We have measured oxygen permeability of cubic zirconia filters in the temperature range between 1800°C and 2300°C (Fig. 6 and Fig. 7). The highest temperature used was 2263°C. The filters were exposed to feed gas of oxygen/argon and of steam; the oxygen/argon mix was varied from 2% oxygen to 100% oxygen.

A few filters have been used for repeated measurements, and did not show any significant change from one run to the other.

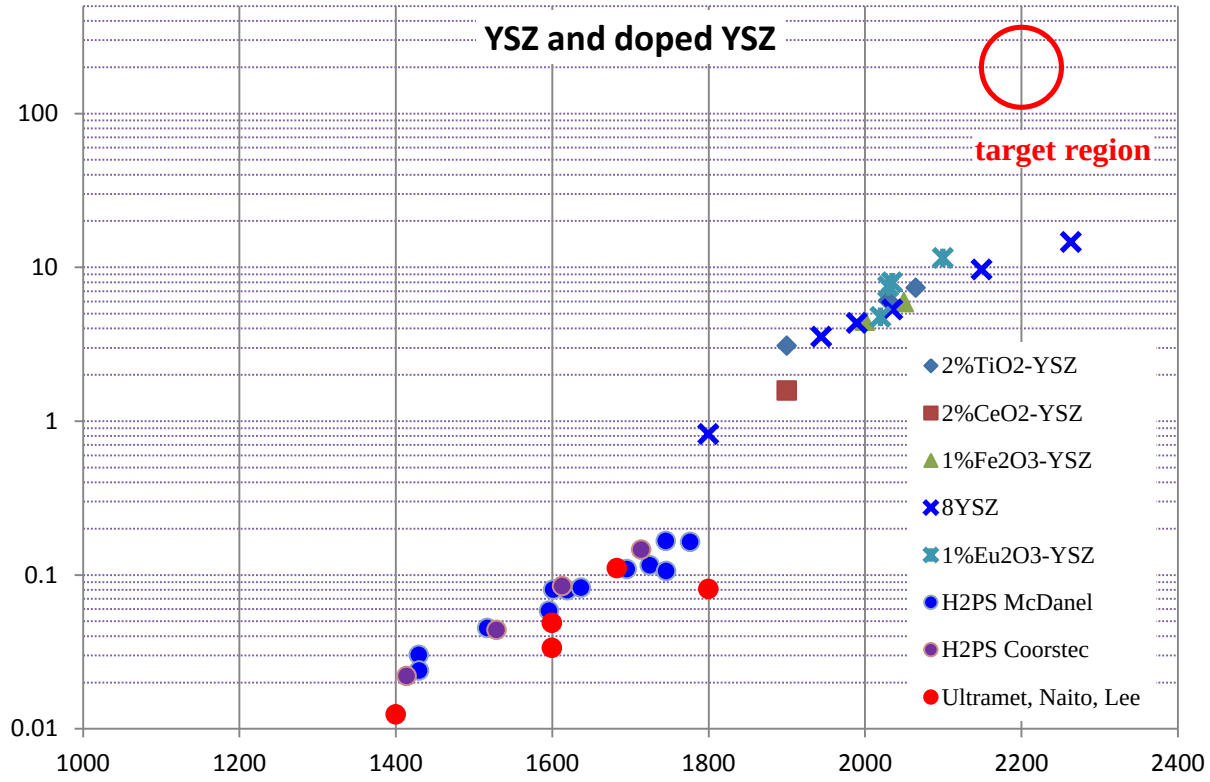

Fig. 6 Oxygen conductivity [S/m] versus temperature [°C] for filters made of cubic stabilized zirconia with and without additional 2% doping. The round symbols show published data of Fig. 5 (left). The new data have been taken with oxygen/argon mixes as feed gas. There seems to be an offset with respect to a simple extrapolation of the published data.

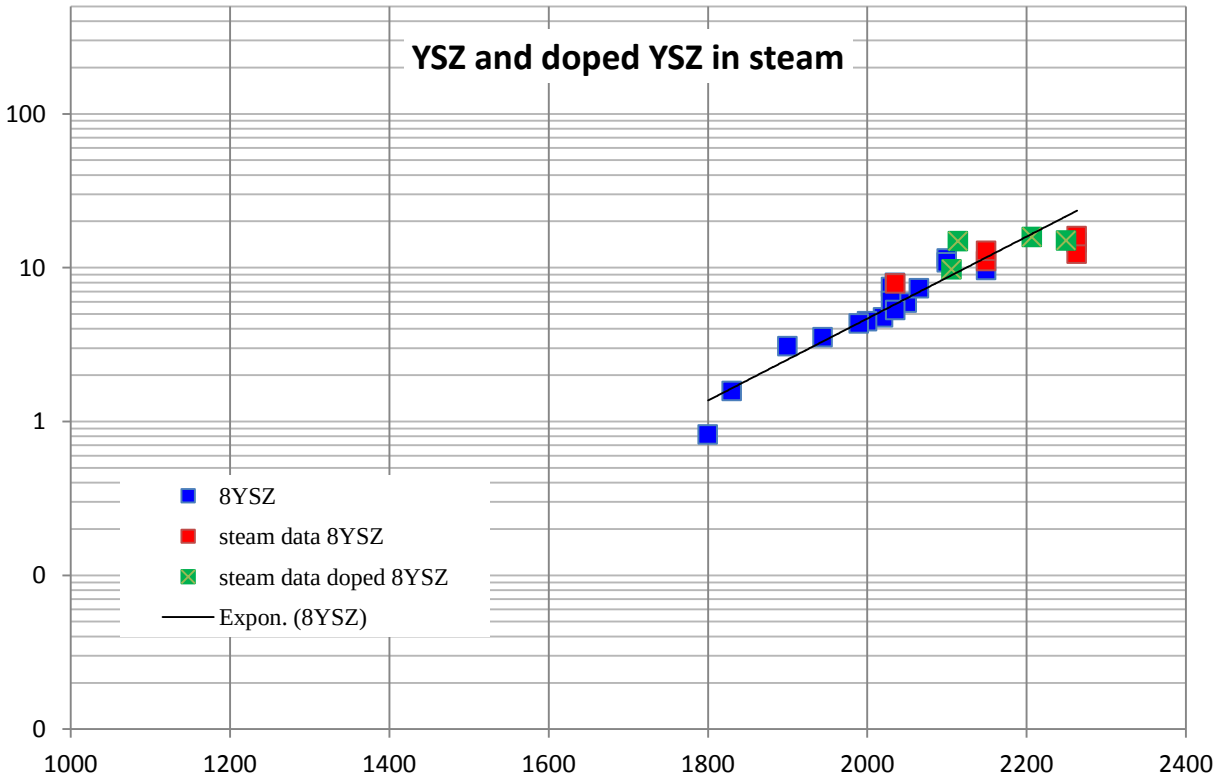

Fig. 7 Oxygen conductivity [S/m] versus temperature [°C] for filters made of cubic stabilized zirconia with and without additional 2% doping. The data were taken with oxygen/argon and steam as feed gas. The solid line is a exponential fit to the data taken with oxygen/argon feed gas.

The data taken with oxygen/argon and steam as feed gas appear consistent, resulting in similar values for the oxygen permeability. The filters stand the highest temperatures but their permeability is an order of magnitude below the benchmark.

B. Gadolinia Doped Ceria

Gadolinium-oxide doped ceria ("GDC" or "CGO") belongs to a class of doped ceria compounds with ionic conductivity exceeding yttria stabilized zirconia electrolytes. Like YSZ, CGO is used as electrolyte and base material for dual phase and cermet electrodes in Solid Oxygen Fuel Cells. In the case of ceria, the doping with Gadolinium gives the highest values of ionic conductivity when dopant concentrations are 10-20% [11].

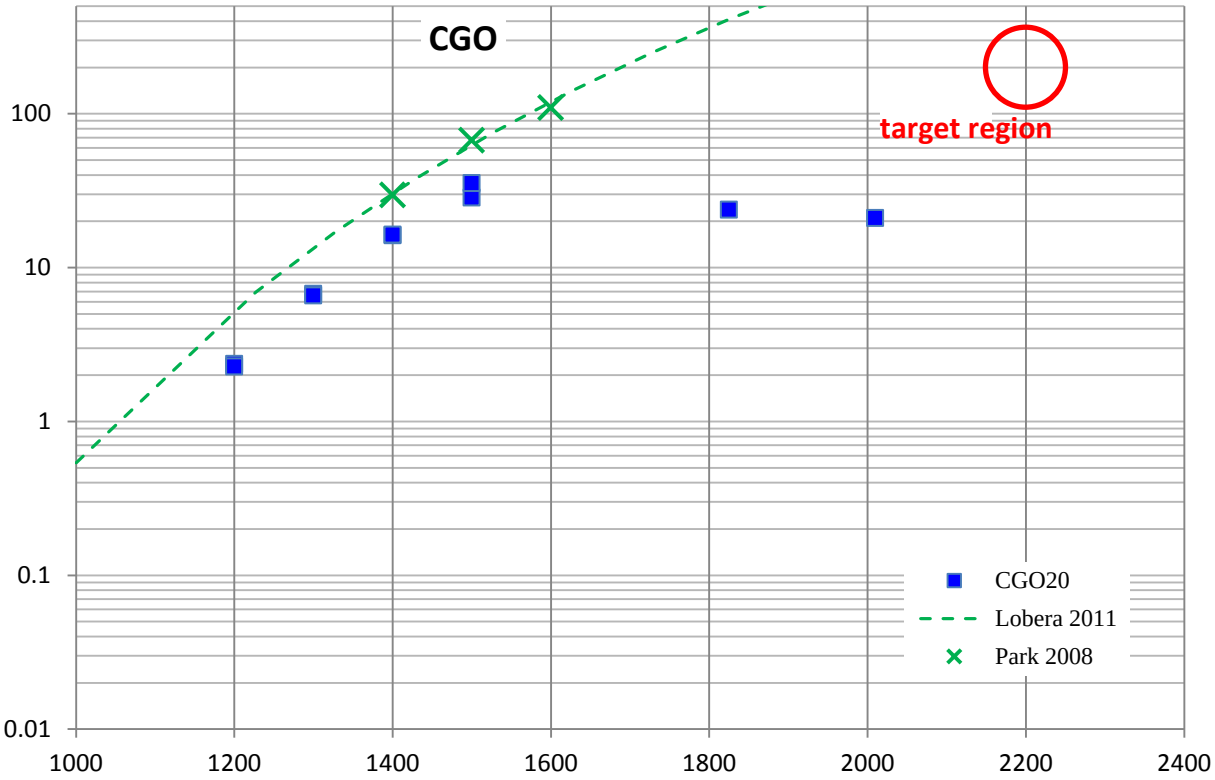

Fig. 8 Oxygen conductivity [S/m] versus temperature [°C] for filters made of cubic CGO20 (i.e., 80% ceria with 20% gadolinia). Data taken with oxygen/argon feed.

The oxygen permeability of CGO20 is much larger, about 20 times larger at 1800°C, than that of cubic YSZ. Our data are somewhat below those of [9] and [10] due to uncorrected feed depletion and permeate flow loss ("backflow"). These effects are discussed further below as they occur in all our measurement. Corrections for these effects unfortunately could not be applied.

Already at 1500°C we reach the limits of our apparatus because feed oxygen flow was not enough to saturate the filter: more than 85% of the feed oxygen was extracted. Therefore, oxygen permeability does not increase anymore at 1800°C. A measurement at 2000°C was attempted but after the run the filter was found deformed which means it had become soft. One filter tube collapsed at 2150°C while being evacuated. At the very high oxygen mobility observed large amounts of Ce^{3+} ions are created (i.e., reduction takes place, the filters turn red) which destabilize the lattice and reduce permeability as well as thermal stability.

Indeed, there are clear indications (discolouring) for strong reduction of the material due to steam. Repair seems possible by exposure to oxygen (cooling in Ar + 2%O_2 environment). However, after reduction and subsequent curing the material becomes brittle and breaks easily. Even without steam, the CGO20 filters became brittle and cracked in regions of high thermal stress (> 50K/cm) at lower temperatures in the region of approximately 800°C to 1500°C.

C. Ceria Doped Cubic Zirconia

Since YSZ is thermally stable and ceria (or rather CGO20) is well filtering, we tested filters made from a combination of the two materials.

The oxygen conductivity of YSZ had been studied by CRMHT Orleans [7]. The co-doping of YSZ with CeO_2 replacing 20% of the ZrO_2 in a cubic crystalline structure was recommended. Such a choice with regard to improved thermal stability and improved oxygen permeability was further corroborated by a number of researchers [12].

A first test with 2% ceria co-doped zirconia had not revealed any significant change with regard to undoped cubic zirconia. The 20% doping, however, gave different results. Our choice of 20% for the ceria was ultimately driven by thermal stability considerations based on the ZrO_2-CeO_2 phase diagram [13]. Furthermore, we maintained an 8% Y_2O_3 doping to further stabilize the cubic structure of the zirconia. Thus, a mix of 80% zirconia and 20% ceria was stabilized with 8% yttria ("Ce-YSZ"). Ceramics processing and filters production was developed and accomplished by Fraunhofer IKTS at Hermsdorf.

The thermal stability compared with the CGO20 filter is indeed improved and the filters could be tested up to 2250°C.

The permeability data are shown in Fig. 9. The feed gas was argon-oxygen mix and was limited due to the test apparatus to a maximum of flow 100 ml/min. For comparison are shown the parameterizations of Lobera for CGO and Lapcique for YSZ together with our fit to the data in Fig. 7.

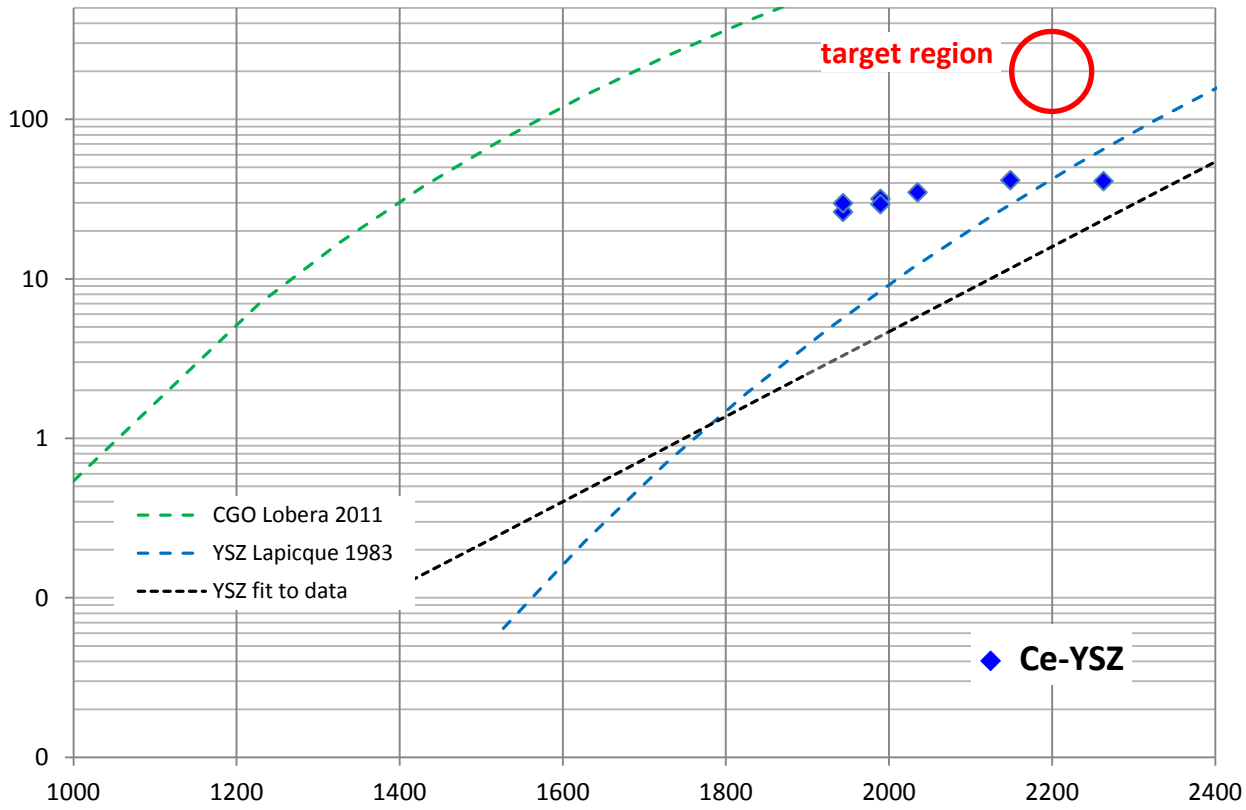

Fig. 9 Oxygen conductivity [S/m] versus temperature [°C] for Ce-YSZ (8% Y_2O_3 + 92% (20% CeO_2 + 80% ZrO_2)). The feed gas was argon-oxygen mix and was limited to a maximum of 100 ml/min. For comparison are shown the parametrizations of Lobera [9] for CGO and Lapicque [7] for YSZ together with our fit to the data in Fig. 7 (dashed lines).

The conductivity of the Ce-YSZ has a comparatively flat slope and levels out. The level lies at around 30 S/m – just like in the CGO test – and indicates the upper limit of our apparatus' capacity to determine permeabilities. Increasing feed gas flow or reducing filter surface was not possible anymore because the project and its resources had reached their ends. The data shown are therefore merely lower limits. However, these limits for the oxygen permeability of the Ce-YSZ are already more than 3 times higher than the measured permeabilities of plain YSZ. They lie at 20% of the benchmark.

With these Ce-YSZ filters we have obtained quite different results in *steam*. In particular, the oxygen permeability at high temperatures is much decreased – an order of magnitude. We think that this is explained by massive backflow (see below) as we not only have the oxygen depletion of the retenate gas but furthermore the effect of oxygen pumping from the residual hydrogen in the retenate. Further experiments will have to clarify this.

V. Sources of Systematic Errors and Operational Limitations

A. *Measurement Errors*

a) We estimate the temperature measurement error at the highest temperatures to typically less than ±10K.

b) The instrument error of the measurement of gas flows and pressures is on the per cent level.

c) According to straight forward gas flow formula, the flow resistance inside the filter tubes and the gas pipes plays a considerable role. There is pressure loss along the pumping line. The data have been corrected for a calculated pressure loss using measured temperature profile along the filters and extraction tubes. The error on the permeate pressure due to backward calculation of flow resistance is estimated to be of the order of 20%. It is less relevant due to the presumed logarithmic pressure dependence of the permeability.

d) The geometry and position of the components inside the protective tube was measured before installation. Thermal expansion wass of the order of a few millimetre for the 32 cm long filter tubes. Also, there remains position uncertainty with regard to the temperature profile and thus with the active filter surface. This adds a systematic error of the order of 15%.

B. *Limited feed oxygen flow and feed oxygen depletion*

a) Depletion inside the feed gas due to extraction is in most cases small. At the high operating temperatures diffusion is much faster than the extraction through the filters. However, at high extraction rates oxygen depletion becomes important.. Indeed we have worked at extraction ratios of well over 50%.
With steam this type of dilution can be ignored because only a very small fraction of about 5% of the molecules dissociates.

b) The gas system was laid out by Fraunhofer IKTS for a maximum O_2/Ar feed gas flow of 100 ml/minute. If all oxygen was extracted, the theoretical maximum oxygen conductivity would be about 38 S/m.
- Because of the setup with gas flow from an inlet near the tip of the filter and an outlet at the bottom of the filter, a fraction of the oxygen will always exit through the outlet.
- The filters act as an oxygen pump. When the possible flow through the filter -because of its high permeability- is of the order of the feed flow or even higher, it occurs that retenate gas is sucked from the outlet line. Also, furnace gas had been sucked through the segment interfaces in the protective tube.[5]

Basically, at high permeability of a filter material, there was not enough oxygen to saturate that filter and what is measured merely is the amount of oxygen supplied.

We have varied oxygen flow by adding argon to the feed gas. We observe a constant result for the oxygen conductivity when the permeability is low (Fig. 11). The slight drop in Fig. 11 is indicative of the feed gas dilution mentioned above. When the permeability is high, the measured permeability scales with available oxygen (Fig. 10).

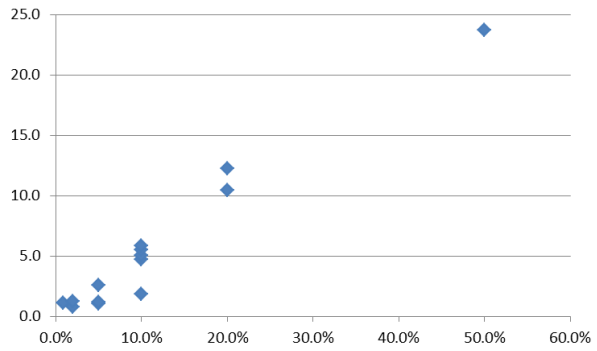

Fig. 10 Oxygen conductivity [S/m] versus O_2 concentration [%] (flux 100 ml/min) temperature [°C] for CGO20 at 1825°K.

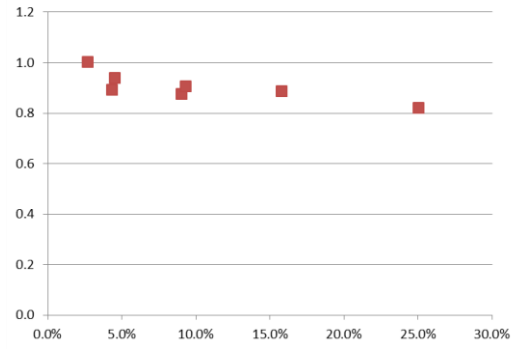

Fig. 11 Oxygen conductivity [S/m] versus O_2 concentration [%] (flux 100 ml/min) temperature [°C] for YSZ at 1800°K.

[5] The composition and segmentation of the protective tube had been optimized steadily throughout the testing. Early test had to be discarded because of the leaking at the intersections. With careful polishing and the reduction of the number of segments, the leaking was much reduced.

Because we looked at these feed gas effects rather late in the project, we have not been able to study them systematically and to derive a correction to the data. In any case, the correction for the permeability would be upwards.

C. Asymmetric feed gas stream

The feed gas is streaming out of its inlet on one side of the filter (Fig. 4). Thus, if there is less oxygen than the filter can take, it filters effectively only in a spot near the gas inlet (Fig. 12), which furthermore is cooled a little because of the somewhat lower temperature of the incoming feed gas.

Our permeability data are calculated assuming a fixed active surface that is determined from geometry and does not take into account feed gas flow, temperature and depletion.

Applying a CFD-based correction[6] to the data based on detailed CFD simulations would increase the oxygen permeabilities in particular at higher temperatures.

[6] A detailed model of the apparatus and CFD simulations had been provided by the engineers of HES-SO/HEPIA/CMEFE in Geneva and PLS Fluid Dynamics sarl. Though we had a model to understand the behavious of the apparatus and the phenomena that were observed, we did not have the resources to do the simulations individual simulations necessary to obtain a correction for the data.

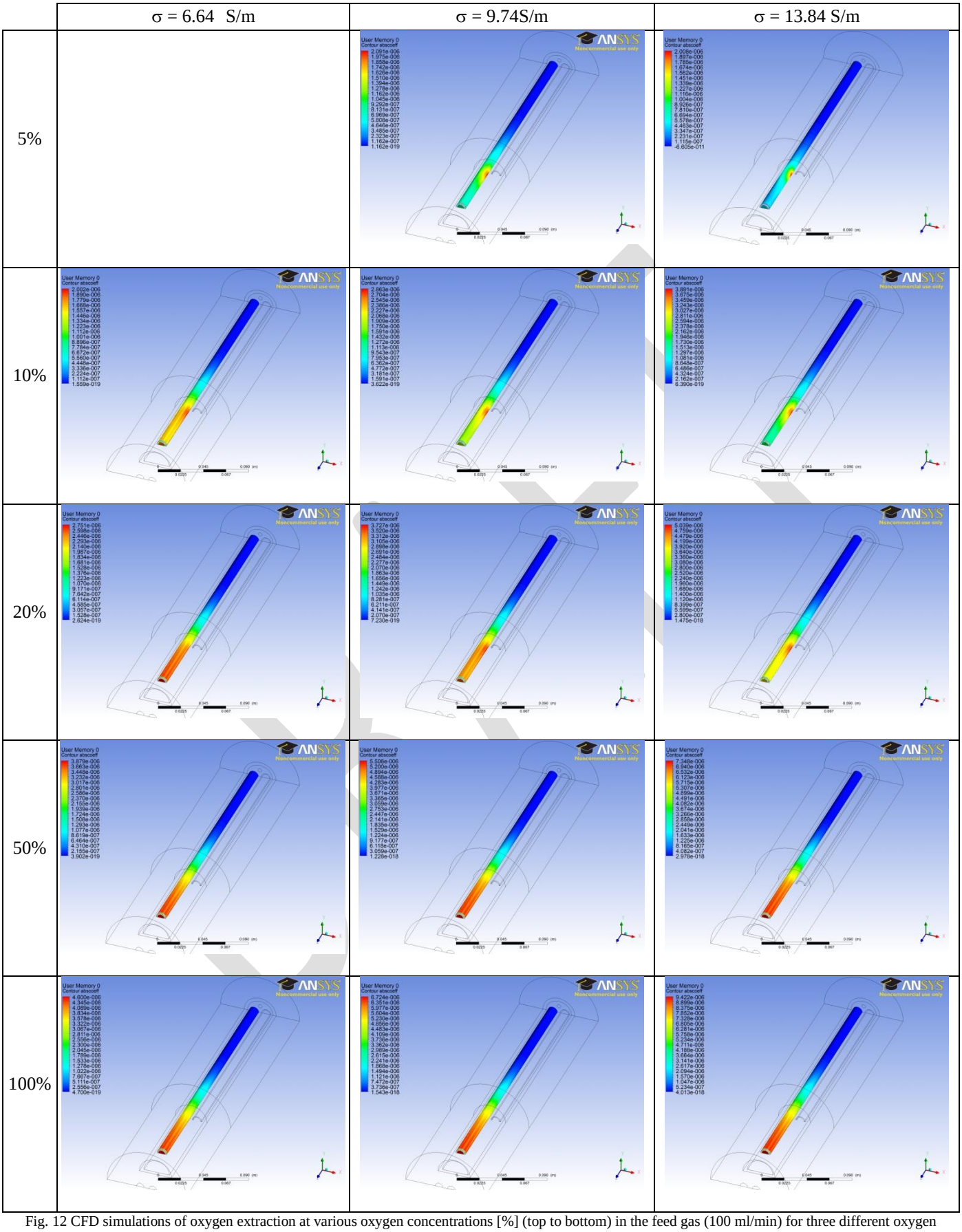

Fig. 12 CFD simulations of oxygen extraction at various oxygen concentrations [%] (top to bottom) in the feed gas (100 ml/min) for three different oxygen conductivities [S/m]. Red = high flux into the filter tube, blue = no flux or even negative flow. The simulations were provided by HES-SO/HEPIA/CMEFE within the thesis of Pierre-Louis Schmitt.

D. Backflow

There is the phenomenon of "backflow" in which already extracted oxygen flows back into the feed gas because outside the hot zone at intermediate temperatures the feed gas is oxygen diluted to a concentration below that of the permeate gas inside the filter tube, which still has residual oxygen permittivity in this region. Backflow is extracted oxygen that returns into the exiting residue gas stream, and thus reduces the apparent, i.e. measured permeability of the material.

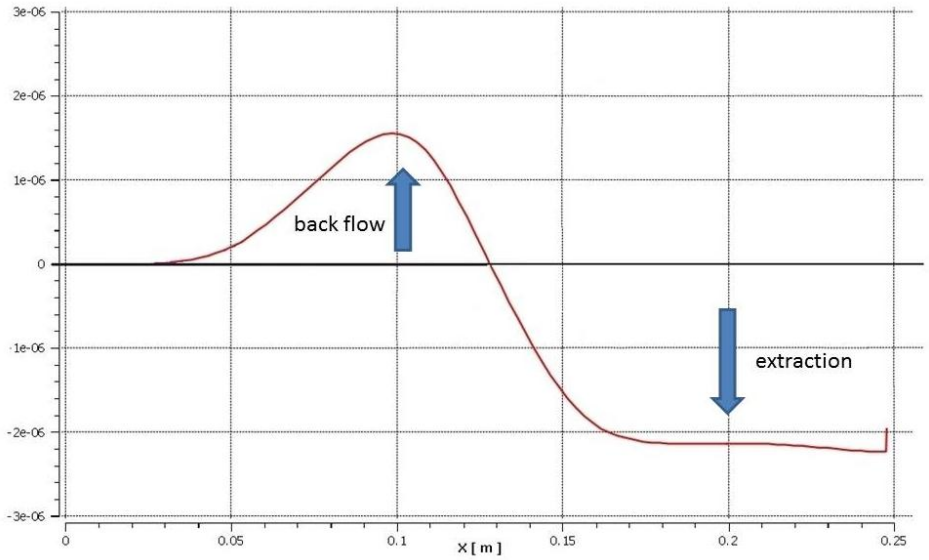

Fig. 13 Simulation of oxygen extraction along the tubular filter from its top at 2250°C (right) to the exit at about 200°C (left). The filter has a length of approx. 25 cm. Oxygen extraction from the feed to the permeate side is negative flow. Backflow in this example is of the order of 30% with a filter that has a factor 10 lower permeability than the Ce-YSZ which was tested in the experiment.

This phenomenon can only occur when the feed oxygen concentration is less than 100%. Of course the lower the more pronounced the effect can be. It is particularly relevant when the feed gas is steam because the oxygen concentration (from dissociation) is very low at the considered operating temperatures around 2500K and furthermore the hydrogen in the residue flow acts as an oxygen pump.

The backflow effect was discovered in CFD simulations [14]. It was only quantified for three example cases and could not be applied as a correction to the data.

The rather large backflow should be inhibited in actual applications. This could be achieved by increasing the wall thickness of the filter in the relevant region. Alternatively material composition may change gradually to lower permeability materials. All this, however, constitutes an additional substantial complication in the production process.

E. Other experimental uncertainties and limitations

a) The measurements were done with thermo-elements, mono and bi-chromatic pyrometers, and via a calibration of the heating power. In particular for the very high temperatures, most pyrometer readings were not usable because of dirt effects (dust on view windows, in view channels, change of surface reflectivity, etc.).The temperature measurement can have occasionally a large systematic error which can be ±30K.

b) The temperature distribution at the hot end of the filter tubes is not quite flat. This is partially because of the furnace geometry, but also because the feed gas is injected via a narrow tube that ends in the hot region; the incoming gas is not quite heated to operating temperature when it exits the inlet tube. For a quantitative correction CFD simulations would be helpful.

c) In many of the experiments argon was used as a carrier gas. Depletion of oxygen or steam was taken into account using series of measurement with varying amounts of argon and extrapolation. Unfortunately not all measurement series went below an argon fraction of 50% in the feed gas which would have been necessary for a good extrapolation.

d) The feed gas flow and turbulences inside the setup can only be revealed by CFD simulations.

e) Although yttria has compared to zirconia a rather low oxygen permeability. We have not taken into account oxygen loss from the feed gas into the furnace atmosphere through the protective tube.

f) Due to the furnace concept with the segmented protective tube, furnace argon leaked into the feed gas space at the intersections of the segments. Furthermore, due to residual and leaking oxygen and steam, carbon dioxide and monoxide formed outside entered the feed gas. In the course of time, these problems were experimentally reduced, but we cannot quantify them. We think, however, that the measurement series with their extrapolations eliminated a large fraction of the effects due to contamination with furnace gas.

All points lead to the measured permeability being an underestimate of the actual, real permeability.

VI. Conclusion and Outlook

A test bench that allows ceramic filter testing with oxygen and steam feed gas up to and beyond 2200°C had been developed. It provided meaningful measurements of oxygen permeability of some ceramics materials. Eliminating the various imperfections and dealing with physical and chemical phenomena to obtain improved data requires substantial revision of the test bench and associate equipment. Furthermore, measurements should be accompanied by detailed fluid dynamics simulations not only to improve the understanding of the behaviour of the apparatus but also to be able to quantify phenomena and apply appropriate corrections to the measured data.

Cubic stabilized zirconia exhibits good thermal stability with oxygen permeability increasing with temperature. However, the permeability at 2250°C is roughly a factor ten below that needed for making an economically interesting solar thermal water splitting reactor for hydrogen production. Doping at the 2% level did not change this situation significantly.

Oxygen permeability data for other filter materials, together with observations of their thermal stability have been obtained up to 2250°C. While ceria (or doped ceria) is not sufficiently stable, and stabilized zirconia is not sufficiently filtering, a combination of the two materials might do the job. In a first attempt we have demonstrated gain of at least a factor four by co-doping cubic zirconia with ceria. However, measurements of high permeabilities were flawed by limitations from the apparatus and can only be considered lower limits.

Dopants like La, Sm, Yb, and Sc replacing the Y might increase the oxygen conductivity of cubic zirconia. Other ceramic structures involving La_2O_3, e.g. LaSrFe compounds or zirconia based perovskites should be examined for their thermal stability and oxygen permeability above 2000°C. There is very little known and much to be discovered.

We regret that means and time did not allow for a more comprehensive study of this subject.

References

[1] Int. J. Hydrogen Energy, Vol. 22 (1997) pp. 481-486, Vol. 23 (1998) pp. 89-98, Vol. 25 (2000) pp. 739-745, and Vol. 25 (2000) pp. 1043-1050.
[2] In the course of the development of a protective tube we have experimented with zurconia, hafnia-zirconia and yttria tubes from various suppliers. Hafnia is expensive and zirconia exhibits oxygen permeability. After trails with varying grains sizes and production methods the yttria tubes were slip-cast by Porzellanfarbik Hermsdorf GmbH , pre-cut by Fraunhofer IKTS both at Hermsdorf, Germany, and finished by Stecher Ceramicparts at Uetendorf, Switzerland.
[3] We observed two problems which lead to the destruction of the protective tubes. The first was reduction on the outside due to the argon atmosphere needed to protect the graphite heating elements. The second was the segmentation which allowed some feed gas –oxygen or steam- to exchange with the furnace argon, react with the graphite and thus act as a vector for carbon to reach the oxide ceramic parts which consequently got, faster or slower, destroyed.
[4] ULTRAMET provide data for their products which include oxygen permeability data of zirconia at temperatures up to 1800°C. Available: http://www.ultramet.com/ceramic_protective_coatings.html#refractory_ox (last checked 28/02/2017).
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