Solar Thermal Hydrogen Production - A Challenge

Activities of Creative Services within the development of a thermal hydrogen generator.

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Creative Services has, together with Nils Kongmark, invented a method to produce hydrogen from water and heat efficiently and cheaply. The method was patented[1] in 2003 with two more patents in 2004 and 2006 covering the "H2P Technology" based on that method. Creative Services and Nils Kongmark had sold this intellectual property to H2 Power Systems Ltd. and eventually got engaged to oversee the development of a hydrogen generator between 2010 and 2013.

Hydrogen production from water and heat is nothing new, and had been explored in the past. Hydrogen is known since 1766 (Cavendish) and electrolysis since around 1800. Research on direct thermal water decomposition (splitting) was pursued in the 1960s in an attempt to increase the efficiency of hydrogen production processes. This research got a strong boost during the oil crisis in the 1970s. However, the then available gas separation techniques and materials pushed research in the direction of multi-step processes, avoiding the need for very high temperature materials and simultaneous gas extraction. The efficiency of these processes is comparatively low and they do not appear to be economically interesting. This fact and that cheap oil and natural gas was again available, led to a world-wide decrease in interest and funding for thermal water splitting from the 1980s. Most recently, which was in the 1990ies, Prof. Abraham Kogan of the Weizmann Institute had done a lot of development work using solar heat for directly producing hydrogen from water.

The worries about peak oil and the impact of the use of fossil resources on the climate have, however, steadily increased leading most prominently to the creation of the IPCC[2] and its annual reports. Hydrogen as fuel would be an ideal solution for eliminating carbon emissions as its consumption results only in water (steam). But although hydrogen is found abundantly on our planet, it is always tied to other atoms: to carbon in fossil fuels or to oxygen in water. Getting the hydrogen off the carbon and oxygen economically was the challenge in the past. Steam reformers produce hydrogen at industrial scale, but consume fossil fuels e.g. natural or bio gas, and come with the related emissions[3]. Today hydrogen should be produced in a sustainable and environmentally acceptable way. To use solar power is the logical consequence, either in the form of electricity for water electrolysis or in the form of heat for thermal water splitting. Electrolysis bears the cost of electricity, which makes the hydrogen

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[1] Patent family of PCT/EP2007/005236 (Title: "Reactor with controlled thermal gradient for the production of pure hydrogen"), Patent Family of PCT/IB2004/052827 (Title: "Reactor for the simultaneous separation of hydrogen and oxygen from water") and Patent Family of PCT/FR03/01454 (Title: "Method for producing pure gases, in particular hydrogen and oxygen"), now owned by H2 Power Systems Ltd., Dublin, Ireland.

[2] IPCC - Intergovernmental Panel on Climate Change (www.ipcc.ch) Fifth Assessment Report: "*Integrated and sectoral studies broadly agree that opportunities for switching to low-carbon fuels exist in the near term and will grow over time. Methane-based fuels are already increasing their share for road vehicles and waterborne craft. Electricity produced from low-carbon sources has near-term potential for electric rail and short- to medium-term potential as electric buses, light-duty and 2-wheel road vehicles are deployed. Hydrogen fuels from low-carbon sources constitute longer-term options.*"

[3] For steam-methane reforming, in the ideal case, the carbon (CO_2) emissions are 6.6 Kg for each kilogram of hydrogen produced.

expensive. Exploiting solar heat could be much cheaper, and this is what the development was aiming for.

The inventors had shown that on a theoretical basis rather high conversion rates from heat to hydrogen could be achieved with a two membrane generator extracting simultaneously oxygen and hydrogen from dissociating steam. Such a device would have no moving parts. It could be built rather cheaply. Using free solar energy, the hydrogen would in turn be cheap. The estimates indicated competitiveness even with hydrogen from fossil resources e.g. steam reforming.

Studying documentation and publications, and talking to experts, Creative Services found out rather quickly that although producing hydrogen from water and heat is possible, the material challenges due to the high temperature required in the process had not been overcome and devices built so far were all experimental installations for research and far from any economic viability.

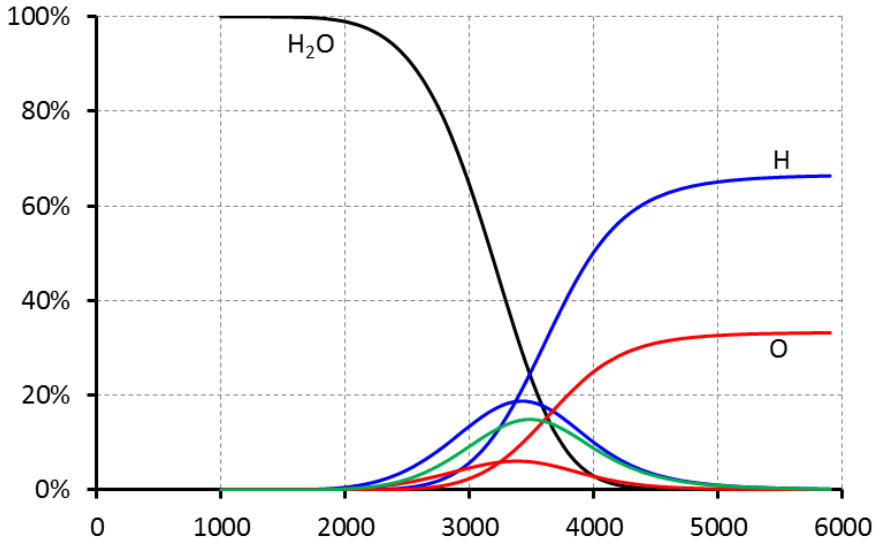


Figure 1 Water dissociation as a function of the absolute temperature in Kelvin (1°C =273.15K) at 1 atm system pressure. Below about 1800K (1500°C) the water molecule H_2O rests intact. Above this temperature, some of the water molecules can break up in O, H, OH and H_2. These fragments can recombine into H_2O or they can form new molecules like O_2, H_2O_2 or HO_2 of which essentially only the oxygen O_2 occurs in sizeable quantities. The formation of "intermediary" molecules has a maximum at around 3400K (3100°C). At higher temperatures even these molecules split and at the very highest temperatures only the hydrogen (H) and oxygen (O) atoms can exist.

The latter had been covered in the three patents[1]. Initial considerations and calculations indicated that the conversion rate heat-to-hydrogen, theoretically close to 90%, could be of the order of 65% practicably. This is very advantageous over other solar hydrogen generation technologies (electro-chemical, photo-chemical, biological…) which have practical difficulty reaching beyond 5%. Fully optimized, hydrogen generation based on the H2P Technology would compete with electrolysis and steam reforming[4].

[4] The specific energy consumption for a typical commercial steam methane reforming process is of the order of 13 MJ/Nm^3 on the low heating value basis. This translates into approximately 45 KWh/Kg H_2. Refining Processes Handbook; Gulf Publishing Company: Houston, TX, 2008.

The optimal operating temperature for employment in a viable generator is 2500 K i.e. 2227°C. Finding the right materials to build a device was the remaining challenge.

Creative Services was engaged by H2 Power Systems (H2PS[5]) for managing the development of a hydrogen generator. The strategy to get to a functioning device was imposed by the circumstances: Firstly develop appropriate materials for the high temperatures in the process, and -due to the lack of expertise in the field- also develop the equipment needed in the development of these materials. Once materials were found, a hydrogen generator could be built.

Material	Melting Point	Material	Melting Point	Material	Melting Point
$ErCrO_3$	2300°C	SrO	2430°C	MgO	2852°C
Nd_2O_3	2300°C	Lu_2O_3	2470°C	W_2C	2860°C
$SrZrO_3$	2300°C	$LaCrO_3$	2470°C	UO_2	2870°C
La_2O_3	2285°C	CeO_2	2500°C	NbB_2	2900°C
VN	2320°C	BeO	2507°C	TiB_2	2940°C
Tb_4O_7	2330°C	$CaZrO_3$	2350°C	WB_2	2900°C
Sm_2O_3	2335°C	$SiZrO_4$	2550°C	TiN	2930°C
Dy_2O_3	2340°C	NbN	2573°C	BN	2967°C
Eu_2O_3	2350°C	CaO	2580°C	WC	2970°C
B_4C	2350°C	$BaZrO_3$	2620°C	ZrN	2980°C
$MgCr_2O_4$	2350°C	UN	2630°C	TaB_2	3000°C
UC_2	2375°C	ThC_2	2655°C	ZrB_2	3040°C
$Tm2O_3$	2410°C	Mo_2C	2687°C	TiC	3140°C
Er_2O_3	2364°C	MoC	2692°C	ThO_2	3235°C
Ho_2O_3	2395°C	$Sc_2Zr_2O_7$	2700°C	HfN	3305°C
Cd_2O_3	2395°C	SiC	2730°C	TaN	3360°C
Gd_2O_3	2385°C	ZrO_2	2715°C	NbC	3500°C
Yb_2O_3	2420°C	B4C	2763°C	ZrC	3540°C
Y_2O_3	2410°C	HfO_2	2790°C	TaC	3880°C
Sc_2O_3	2450°C	VC	2810°C	HfC	3890°C

Table 1 Selected high temperature materials and their melting points. For use in steam only few materials are appropriate, basically oxide ceramics. The high melting point oxides urania (UO_2) and thoria (ThO_2) are radioactive.

The check of the properties of high temperature materials comprised the following basic aspects:

- Is the melting point high enough?
- Is the material chemically stable in steam at 2500K? Does it react? Does it evaporate?
- Has the material conductive property? What is its steam/oxygen/hydrogen permeability?
- Is the material mechanically stable? Where is its Tammann temperature? Does it undergo phase transitions during in heating process? Does it develop a glassy phase?
- Will parts made from the material support high thermal stress from thermal gradients during the heating up and cooling down phases? What is the favourable microstructure (grain, pore size distribution)?
- Can such parts be made gastight? Can they be made with high open porosity?

[5] www.h2powersystems.com

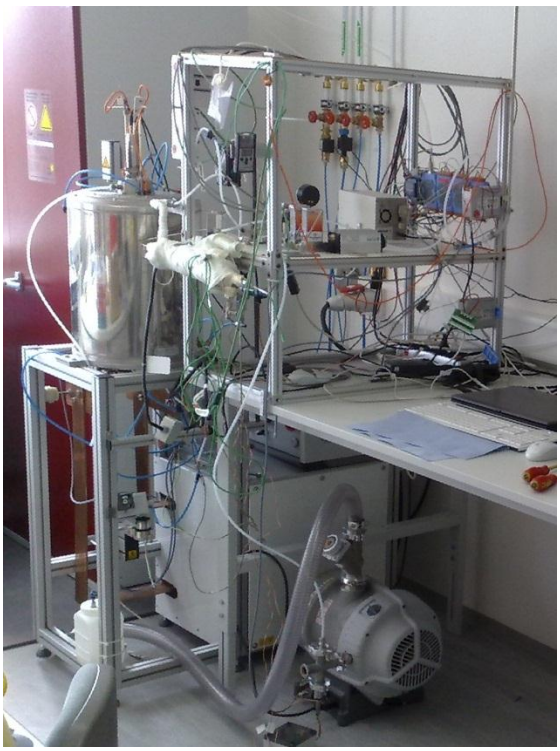
Conventional knowledge of material properties ends around 1600°C. Anything above is extrapolation, hypothesis, and in the best cases the qualitative experience of someone who worked with the material at the high temperatures. Creative Services collected information in discussions with furnace makers and refractory ceramics specialists across Europe. Basically, only zirconia (ZrO_2) and the more expensive hafnia (HfO_2) were recommended as sole materials potentially suitable to the thermal water splitting reactor.

What also came out in the discussions and studies was that there is no equipment available for the testing of materials at the high temperatures in steam. Based on the experience with an exploratory high temperature furnace built with Swerea/IVF[6] during the years 2007/2008, Creative Services suggested developing a test bench, what was accepted by H2PS. During 2010 a collaboration with Fraunhofer Institute for Ceramic Technologies and Systems (IKTS[7]) was set up.

Materials for oxygen filters

The test bench is basically a tubular furnace in which the region with the operating gas is separated from the heating parts by a ceramic tube. Tests are performed on samples inserted into the protective tube.

The design of the test bench allowed for thermal gradients up to 200 K/cm along the ceramic tubes, and that created considerable problems. Various materials and configurations were tried until a solution for the protective tube was found with which tests in steam up to 2250°C could be performed.



[6] www.swerea.se
[7] www.ikts.fraunhofer.de

Figure 2 The test bench at IKTS. The actual furnace is the small barrel on the left. Mounted in the rack are various sensors and detectors. Below the table are power supply and pump. The test bench reaches beyond 2200°C. Data have been obtained up a temperature of 2263°C with both steam and argon/oxygen as operating gas. The test bench was moved from IKTS to H2 Power Technical Center[8] in Geneva in 2014.

IKTS produced the ceramics components, the protective tube and sample tubes made from the materials to be investigated. During two years of operation of the test bench, over 500 data points on oxygen permeability were measured for seven different materials: two single oxides and five compositions. In parallel, a mass of qualitative information on thermal stress behaviour and chemical reactivity was acquired.

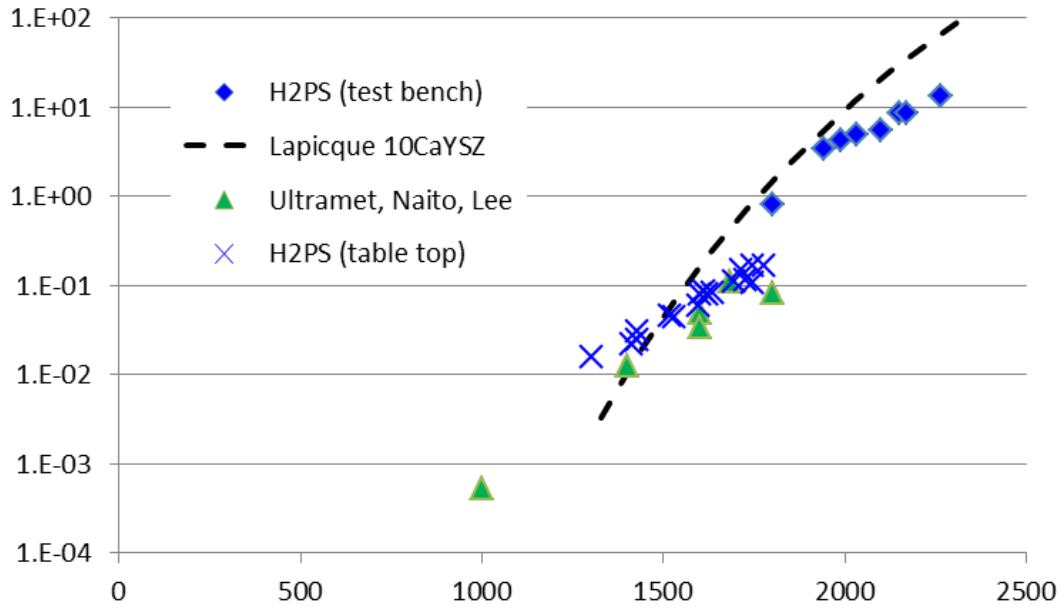


Figure 3 Example of oxygen conductivity measurements for cubic zirconia. The horizontal and vertical axes are in units of °C and S/m, respectively. The green triangles show published data; the dashed line is an extrapolation published in 1983 based on data measured up to 1627°C. Blue crosses represent the data measured with the first furnace (table top, cross) in 2008 and the test bench (diamonds) in 2012 and 2013. The data have systematic errors that have not yet been quantified properly.

The study of the oxygen permeability of materials for filtering at 2250°C has just begun.

The starting point was cubic zirconia, as suggested by a number of people. The results presented in Figure 3 indicate the testing possibilities with the test bench. H2PS had tried doping the cubic zirconia to modify certain characteristics e.g. electron donors to increase electronic conductivity, atoms with different size to modify the ionic mobility. The measurements, within the experimental uncertainty, did not reveal the changes that were hoped for. However, these first doping attempts were overly cautious using very small doping fractions. A more courageous doping in higher fractions and with other atoms will be more revealing. Work left to be done.

Further measurements where done with materials that are known to be very good oxygen conductors at lower temperatures, knowledge mainly deriving from the development of Solid Oxygen Fuel Cells. Two materials were tested. Indeed much increased oxygen permeability was found: material 1 had two orders of magnitude better oxygen permeability when compared to cubic zirconia while material 2 was still a factor five better. However, material 1

[8] H2PTC is located on the premises of the engineering university HEPIA in Geneva, see website of H2 Power Systems.

became soft somewhere between 1800°C and 2000°C while material 2 could stand the 2250°C for a while but became brittle with segregation patterns in regions of high thermal stress (Figure 4). There are more options and these measurements reveal the direction in which to proceed.

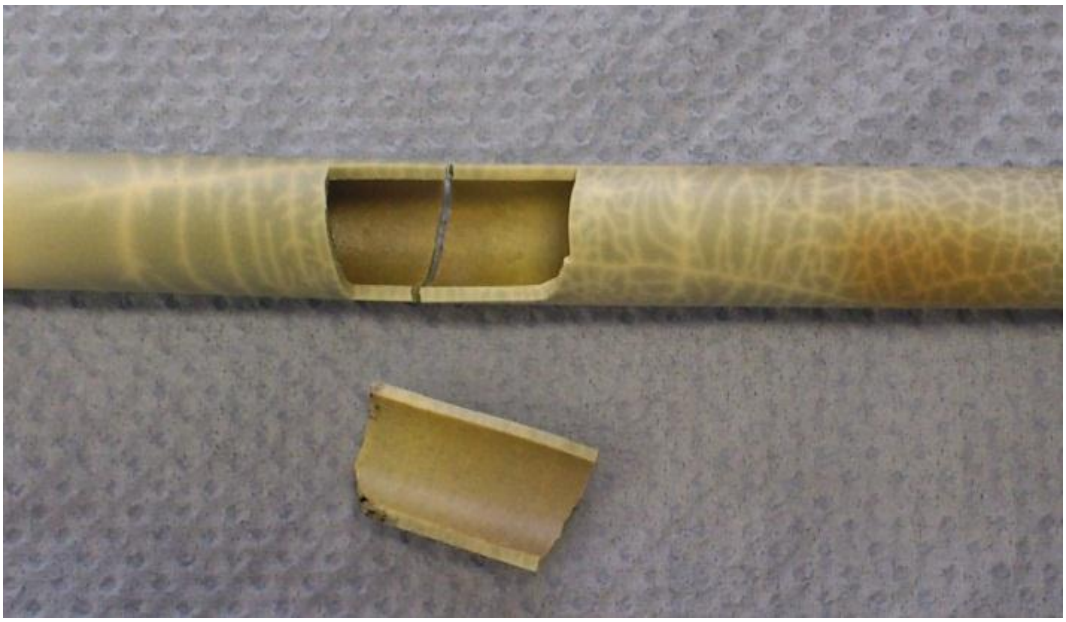


Figure 4 Stress pattern and cracking observed in a region with a high thermal gradient but a comparatively low absolute temperature.

In conclusion, the test bench has demonstrated its capacity to provide oxygen permeability data up to 2250°C from steam and argon-oxygen atmosphere. Certainly, the test bench can be improved after so much learning during more than two years of operation.

Computational Fluid Dynamics (CFD) simulations were begun. Such CFD calculations help to understand the things that are on-going inside the test bench and thus help to reduce the systematic errors and get better data. Full 3D simulations for each experimental configuration are desirable since otherwise crude estimates have to be used to approach parameters like the detailed temperature distribution inside the test bench or the exact composition of the test atmosphere.

Hydrogen generation from heat and steam

Based on the findings from the test bench, Creative Services suggested to H2 Power Systems to build a hydrogen generator by extension of the test bench with a compartment holding hydrogen filters.

The purpose of such a setup was straight forward: proof of concept of the method, in particular the physics/chemical model that had been employed in the argumentation for the hydrogen generator.

In the conception of the hydrogen generator the ideas expressed in the patent of 2004 were followed. Although heating was external and not internal as required by the method (patent of 2003), the core concept of the arrangement hot oxygen filters → hydrogen permeable insulation → cooler hydrogen filters could be tested. The hydrogen filters for the test were

obtained from Energy Research Center of the Netherlands (ECN[9]). These filters are palladium based and work between 350°C and 650°C. The furnace was built by HTM Reetz GmbH and the ceramics were provided, as already for the test bench, by Fraunhofer IKTS. The hydrogen generator was assembled at IKTS and the tests were done there.

The hydrogen generator "POC" was designed during winter 2011/12. The furnace was constructed during spring and delivered to IKTS in March 2012. IKTS added the gas system, in particular steam injection, and hydrogen and oxygen extraction and analysis.

Similar to the test bench, the POC employed a protective ceramic tube separating working gas (inside) from the electrical heating (outside). A serious complication was the extension with a compartment for the hydrogen filters. While in the test bench the hot ceramic parts are one-end-closed tubes which could expand freely, in the POC both ends of a long tube are fixed because at the one end the oxygen and at the other end the hydrogen filters are employed. The thermal expansion and the related stress caused considerable problems and various measures mitigating the effects had to be implemented. Finaly data could be taken, but the setup still leaves much to be improved.

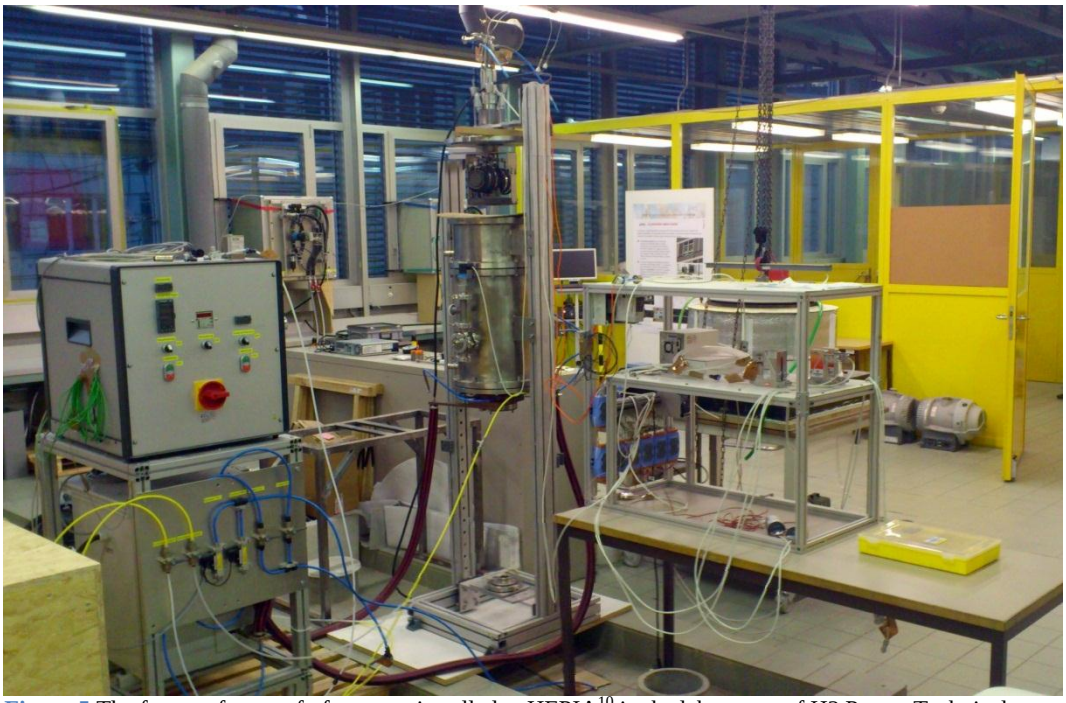


Figure 5 The furnace for proof of concept installed at HEPIA[10] in the laboratory of H2 Power Technical Center in 2014. At HEPIA, compared to IKTS, much more lab space was available for the installation. The hydrogen generator is mounted in the alu-profile rack in the middle of the picture.

Hydrogen was produced for the first time in August 2012 (Figure 6). Due to the problems with the protective tube, which was leaking from time to time, hydrogen production was biased systematically. However, the onset of simultaneous oxygen and hydrogen production between 2000°C and 2100°C is clearly observed. Hydrogen (units Nml[11]) produced was roughly 1.5 times more than that of oxygen, approximating the stoichiometrically expected ratio of two.

[9] www.ecn.nl
[10] www.hesge.ch/hepia
[11] normal millilitre i.e. 1 cm³ of gas at normal (ambient) pressure and temperature.

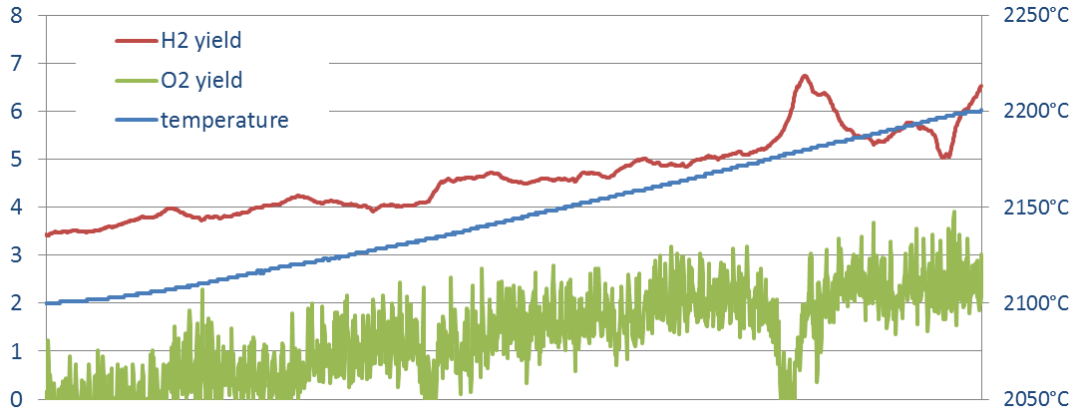


Figure 6 Hydrogen and oxygen extraction (in units[11] of Nml/min, left scale) increases with increasing temperature. The dip of oxygen production and correlated increase in hydrogen production around bin 1320 occurred when the extraction pump of the oxygen extraction system stalled.

Due to various reasons the next and so far the last test of hydrogen production could only be done in June 2013. Hydrogen production was observed, but the experimental circumstances e.g. power fail due to a storm, leaking of the protective tube, did not allow a good measurement.

All in all, the tests with the POC demonstrated that nature works as presumed; in particular hydrogen production was in proportion to the oxygen extracted increasing with temperature. Further testing could, unfortunately not be done. The problems with the protective tube were dominating test preparation and execution, and were disturbing the measurements. In a solar hydrogen generator no protective tube is needed, and consequently the problems related to it will not be present.

Historical note: In October 2012 the sponsor of the project went into liquidation and shortly after H2PS ran out of funds. Creative Services strongly regrets that no further work on this interesting and promising technology could be done.