SOLAR THERMOCHEMICAL HYDROGEN GENERATION WITH A 250-KW STRUCTURED REACTOR: EXPERIENCES FROM TESTS AT THE JÜLICH SOLAR TOWER

Thomas Fend[1], Vamshi K. Thanda[1], Jörg Lampe[2], Steffen Menz[2], Stefan Schmitz[3], Gregor Piesche[4], Stefan Berger[4]*

[1]Institute of Future Fuels, German Aerospace Center (DLR), 51147 Cologne, Germany
[2]Department of Energy Technology, University of Applied Science Cologne (RH), 50825 Cologne, Germany
[3]Institute of Solar Research, German Aerospace Center (DLR), 52428 Jülich, Germany[c]
[4]Stausberg & Vosding GmbH, Reichsweg 30, 52068 Aachen, Germany

*Corresponding author e-mail: thomas.fend@dlr.de

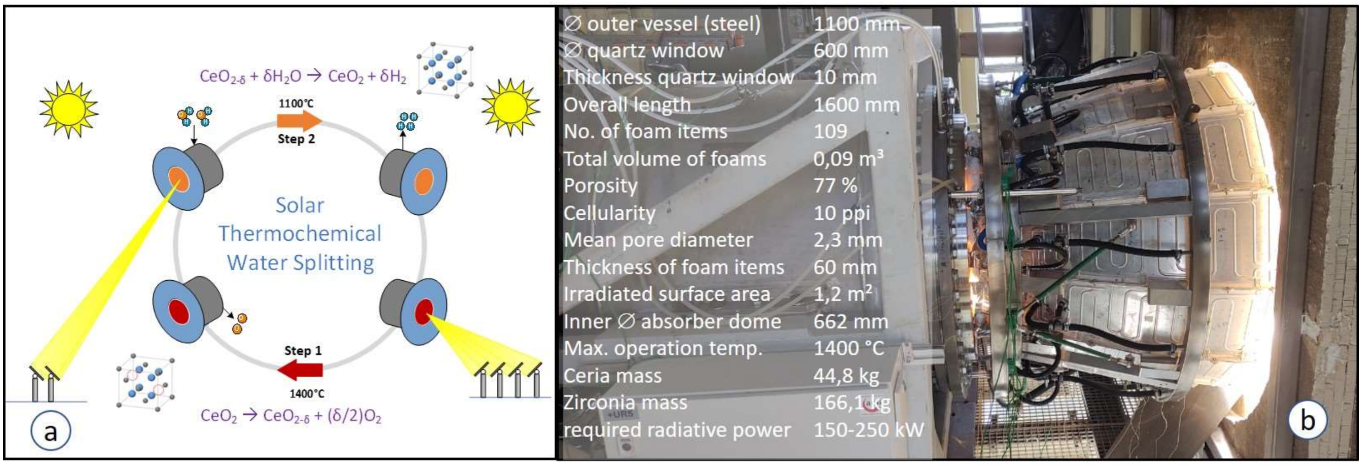
ABSTRACT

Thermochemical water splitting using two-stage REDOX processes and concentrated solar radiation as an energy source has been the focus of process engineering research for more than two decades. It is considered as a promising technology for producing green hydrogen and liquid green fuels at competitive prices in the medium term. In this process concentrated solar radiation is directly converted into storable chemical energy. The present article reports the results of an experimental campaign, which has been carried out at the research level of the Solar Tower Jülich to further demonstrate the feasibility of this technology. Based on the experience from prior tests at a large-scale solar simulator a combined receiver/reactor has been re-designed and built up. The reactor was operated at temperatures between 1200 °C and 1000 °C using radiative power of up to 780 kW generated by part of the heliostat field of the Solar Tower. As redox material ceria has been used which has been coated on a framework of a zirconia foam due to stability reasons. It could be shown that the production of hydrogen in a medium scale structured reactor is possible. The tests also revealed which improvements concerning structure, optical and thermal management as well as operational parameters are necessary to achieve satisfying efficiencies.

Keywords: thermochemical cycle, green hydrogen, redox reaction, ceria, solar hydrogen reactor

1. INTRODUCTION

Solar thermochemical water splitting has been investigated at the Institute for Future Fuels and its predecessor since 2002. Together with national and international partners such as the major research organisations CERTH (Greece) and CIEMAT (Spain) as well as industrial partners such as HELPE (Greece), ABENGOA (Spain) and ENGICER (Switzerland), this technology has been advanced to a great extent. It has high theoretical solar-to-fuel efficiency potential of up to 50% [1, 2] and provides a way to generate hydrogen directly from the sun without prior generation of electricity. A two-stage redox process is used in which a metal oxide is alternately reduced and oxidised, releasing hydrogen in the process (Fig. 1). As part of the NRW projects ASTOR and ASTOR-ST, which have been realized in co-operation with RH Cologne, Stausberg & Vosding and AWS-Technik, this technology has been demonstrated with a 250-kW solar reactor in a large-scale solar simulator [3].



∅ outer vessel (steel)	1100 mm
∅ quartz window	600 mm
Thickness quartz window	10 mm
Overall length	1600 mm
No. of foam items	109
Total volume of foams	0,09 m³
Porosity	77 %
Cellularity	10 ppi
Mean pore diameter	2,3 mm
Thickness of foam items	60 mm
Irradiated surface area	1,2 m²
Inner ∅ absorber dome	662 mm
Max. operation temp.	1400 °C
Ceria mass	44,8 kg
Zirconia mass	166,1 kg
required radiative power	150-250 kW

Fig. 1. The two-stage redox-process with ceria as a functional material (a). The reaction takes place to a certain extent described by the non-stoichiometry parameter δ depending on oxygen partial pressure and temperature in the reactor. (b) Reactor and secondary concentrator in operation on the research level of the Solar Tower Jülich along with some technical data of the receiver.

2. MATERIALS AND METHODS

2.1. Redox material

The redox material used was pure ceria, which appeared as a coating on a zirconia framework consisting of an RPC 10ppi foam produced by EngiCER using the classical Schwarzwalder process. A total of 44.8 kg of ceria and 166 kg of zirconia was used. 109 blocks of slightly different geometry were manufactured, which were then assembled to form the reactor dome shown in Fig. 2d. After the tests in the solar simulator, which totalled 52 operating hours, the entire redox material was replaced with the objective of improving the absorption properties of the reactor. A two-stage porosity was created in each block, in a way that the porosity was higher on the irradiated side to allow deeper penetration of solar radiation (Fig. 2c). Model calculations by RH Cologne have shown that this equalises the temperature in the receiver and thus enables higher efficiency levels.

Some of the material used in the first test campaign exhibited severe traces of degradation, which were particularly evident in strut fractures and detachment of the cerium oxide layer (Fig 2 a and b). The blue colouration at the interface between zirconia and ceria oxide was also conspicuous. X-ray analysis suggests that this is the solid solution $ZrCeO_2$ (Fig 4a), which has been proposed in other studies to improve the reduction properties of the material [4].

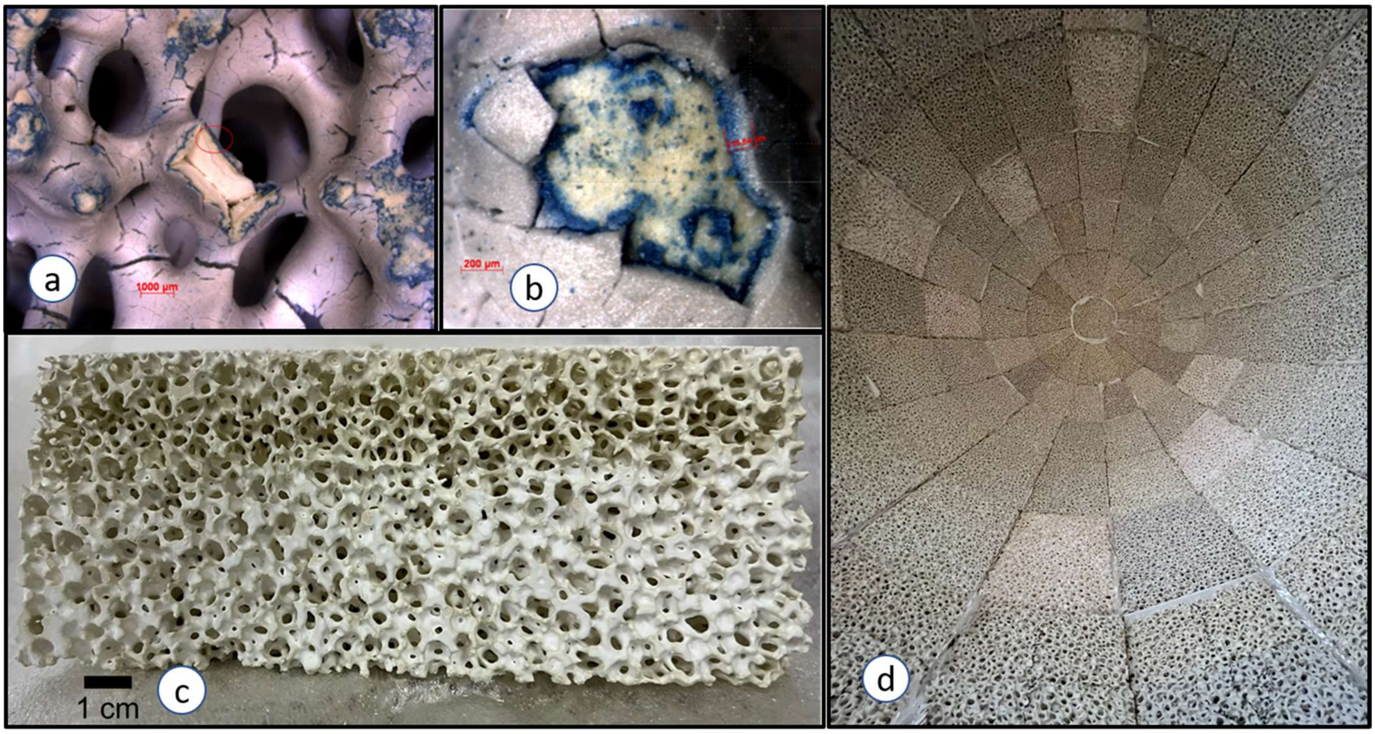


Fig. 2. 10ppi ceria coated zirconia foam used for the reactor. (a) Micrograph of the material after approx. 52 operation hours. (b) Parts of the approx. 135 µm thick ceria-layer detached from the zirconia substrate during tests of the 1st campaign. (c) One of the 109 as received modules of the reactor-dome for the 2nd campaign with two-stage porosity. (d) Front view of the reactor as a whole.

2.2. Experimental set-up

As part of the ASTOR-ST project, we developed a 250-kW reactor, the centrepiece of which was the REDOX dome described in the last section. It can be seen as a further development of the reactors built for the solar gas turbine as part of the EMPOLI and REFOS projects [5], which were also used in a modified form for the solar methane reformation demonstrated in the SOLREF project [6]. The outer vessels of these reactors as well as secondary concentrators with an optical efficiency of up to 80% have been reused, which caused some constraints concerning size and aperture geometry. The reactor is shown schematically in Fig. 3a. An inner vessel separates the incoming and outgoing fluids, which pass the wall of the redox dome from left to right before they finally leave the reactor through the gas outlet. The solar radiation enters the reactor through a flat fused silica window, which replaces the formally used dome shaped version, because the experiment was operated under close to ambient pressure conditions, thus fixing the flat window was easier and the operation safer. Fig. 3b shows a simplified map of the entire set-up. Stausberg & Vosding developed the system control. It consisted of a LabVIEW-controlled PLC that enabled real-time operation and measurement as well as automatic mode and multi reactor operation. During the reduction step the reactor is heated up and flooded with nitrogen 5.0, creating an oxygen partial pressure of 10^{-5} bar provided that the reactor is completely filled up. Only the valves v301, v400 and v500 are open and an O_2-meter monitors the O_2 content of N_2/O_2 mixture leaving the reactor.

Hereafter, v401 is opened and steam enters the reactor to introduce the oxidation step. In the same time v500 is closed, v600 is opened enabling the N2/H2 mixture to leave the system and to be analyzed by a mass spectrometer. The reactor temperature was measured from the rear using thermocouples at a depth of 1.5-3 cm. The whole set-up was put onto the research level of the Solar Tower. In the inserted photograph in Fig. 4c the irradiated reactor can be seen in the middle of the left tower from the outside. The radiative power from the Heliostat-field on the outer aperture of the secondary concentrator was estimated by creating a second similar focus on a white screen equipped with a standard high-flux radiometer.

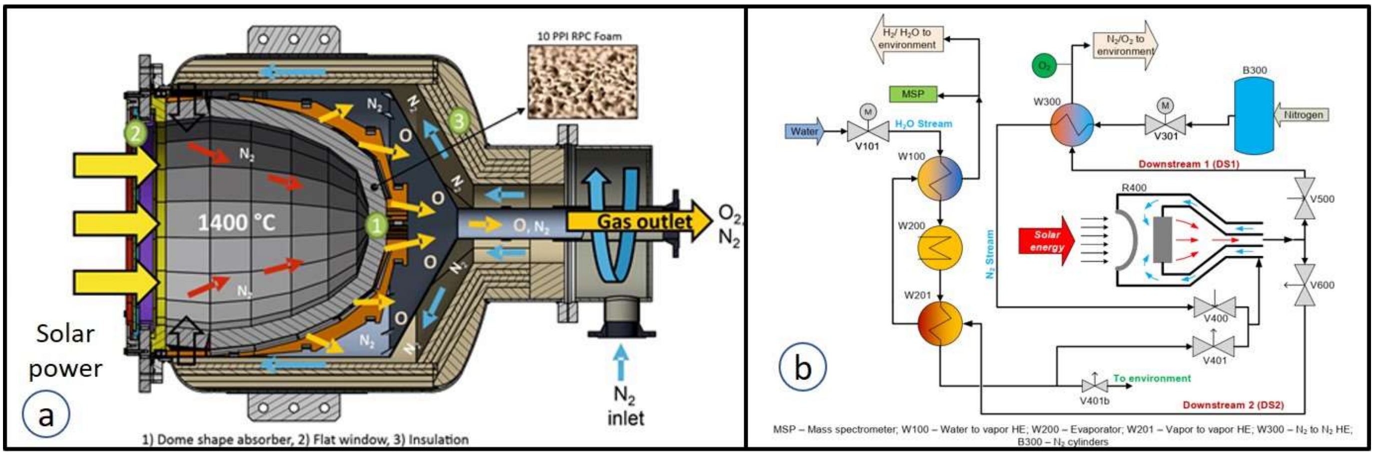


Fig. 3. Schematic representation of the reactor (a) and simplified diagram of the piping and instrumentation for the supply of the reactor with steam and nitrogen as well as the treatment of the outlet gases including three heat exchangers for heat recovery (b).

3. RESULTS AND DISCUSSION

Fig. 4 b and c show the course of an experiment on the research level of the Solar Tower Jülich. On this day, conditions were almost clear sky and up to 285 heliostats each with an aperture area of about 8 m² could be used for the experiment. The blue curve represents the power on the aperture of the secondary concentrator. Due to larger optical losses compared to the mentioned gas-turbine application, only a smaller fraction of this power reached the surface of the reactor. These additional optical losses were caused by a relatively low position of the focus, a horizontal alignment of the reactor and the use of a flat window showing less transmittance due to higher incident angles. The concentration ration was approx. 350. Additionally, reactor average and maximum temperature as well as the steam mass flow is displayed. By successively increasing the radiative power to 690 kW, the reactor was heated up to 979 °C maximum temperature at the backside. At this point a first oxidation phase was introduced resulting in a hydrogen production rate of 0.6 g/h. Once the rate of hydrogen production had fallen to almost zero, a second reduction phase was initiated. Now the maximum available power (780 kW) was put on the experiment. Consequently, the reactor temperature increased and in the subsequent second oxidation phase the hydrogen yield was correspondingly greater and a hydrogen mass flow 1.2 g/h was achieved. However, the reactor temperature did not exceed 1000 °C on the rear. We know from the previous measurement campaign in the solar simulator that the temperature on the irradiated side is significantly higher [3] but the redox foam used during this campaign had a slightly different porosity. From model calculations this effect could be estimated [7, 8] so that we assume that the temperature at the front side was approx. up to 1200 °C. Integration of the hydrogen curve from Fig. 4b provides the absolute values of hydrogen produced during the two cycles carried out. These were 0.2 g and 0.57 g respectively. This is much less then expected but simply be explained by the fact that within this experiment the lay-out temperature of 1400 °C could not be reached by far, because overheating problems with the secondary concentrator and the window flange occurred, which could not be solved in the remaining time of the project. However, the stoichiometry of the reduction equation (Fig. 1a) predicts these amounts for temperatures of 1000 °C and 1080 °C along with a ceria mass of 44.8 kg and an oxygen partial pressure of 10^{-5} bar [9]. Thus, in principle, the reactor is able to generate hydrogen according to predictions based on theoretical calculations and lab scale experimental experiences.

4. CONCLUSIONS

It has been shown that solar thermochemical hydrogen production on a medium scale is possible with the reactor concept developed. The amount of produced hydrogen per mass of redox material used, as predicted by theory, was largely achieved. However, the efficiency of the process in these first tests was relatively low. The main reasons for this are the large aperture to reactor surface area relationship and the associated low concentration ratio. Moreover, the optical efficiency of the secondary concentrator was low. Further work on the optical design of the reactor and the secondary concentrator is planned with the aim of significantly increasing the concentration ratio and thus the overall efficiency.

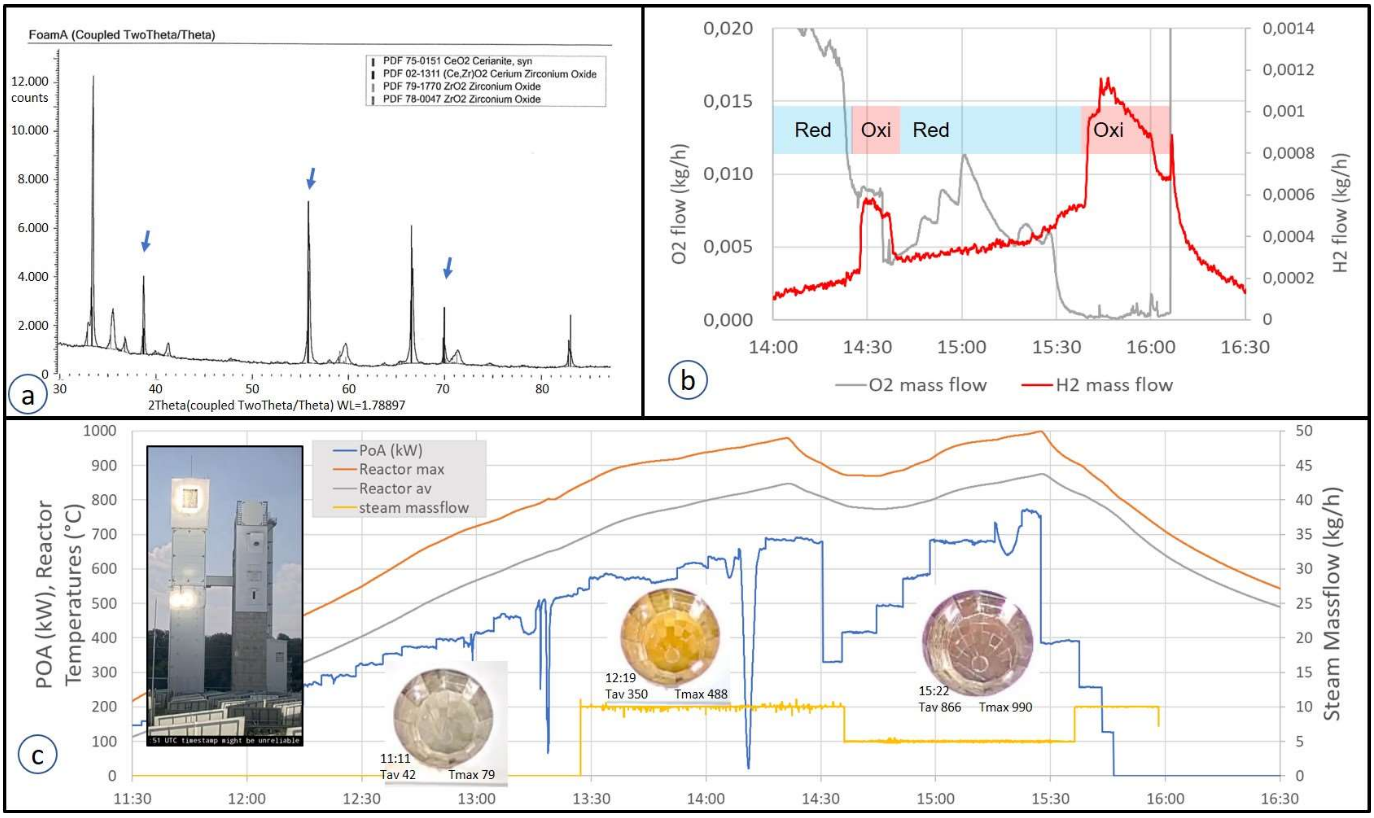


Fig. 4. An X-ray analysis (a) of the degraded material (see Fig. 2) shows the formation of a solid solution (CeZrO2, blue arrows) in the transition region between cerium oxide and zirconium oxide. (b) Oxygen and hydrogen mass flow during the reduction and oxidation phase of the experiment. (c) Related reactor temperatures, radiative power from the heliostat field and steam mass flow. Note that steam was only inserted into the reactor during the oxidation phase by opening valve V401and closing the by-pass V401-b

ACKNOWLEDGEMENT

The study has been carried out in the frame of project ASTOR-ST (EFRE-0801815). The funding of the EFRE fund and the NRW Ministry of Economic Affairs, Innovation, Digitalisation and Energy is gratefully acknowledged

REFERENCES

1. Steinfeld A and Palumbo R. 2001. Solar Thermochemical Process Technology. In Encyclopedia of physical science & technology*, 2001, Edited by* Meyers RA, Academic Press, 15, 237-256.
2. Call F. 2014. Investigation of Ceria based redox materials for thermo-chemical solar fuel production. 2014. PhD thesis. Aachen RWTH.
3. Thanda VK, Fend T, Laaber D, Lidor A, von Storch H, Saeck JP, Hertel J, Lampe J, Menz S, Piesche G, Berger S, Lorentzou S, Syrigou M, Denk T, Gonzales-Pardo A, Vidal A, Roeb M and Sattler C. 2022. Experimental Investigation of the Applicability of a 250 kW Ceria Receiver/Reactor for Solar Thermochemical Hydrogen Generation. Renewable Energy.198:389-398.
4. Bulfin B, Call F, Vieten J, Roeb M, Sattler C and Shvets IV. 2016. Oxidation and Reduction Reaction Kinetics of Mixed Cerium Zirconium Oxides. J. of Physical Chemistry.120:2027-2035.
5. Buck R, Bräuning T, Denk T, Pfänder M, Schwarzbözl P and Tellez F. 2002. Solar-Hybrid Gas Turbine-based Power Tower Systems (REFOS). Journal of Solar Energy Engineering (ASME). 124(1): 2-9.
6. Agrafiotis C, von Storch H, Roeb M and Sattler C. 2014. Solar thermal reforming of methane feedstocks for hydrogen and syngas production - A review. Renewable and Sustainable Energy Reviews. 29:656-682.
7. Menz S, Lampe J, Krause J, Seeger T and Fend T. 2022. Holistic energy flow analysis of a solar driven thermo-chemical reactor set-up for sustainable hydrogen production. J of Renewable Energy. 189:1358-1374.
8. Lampe J, Henke S, Menz S and Fend T. 2024. Solar-driven thermochemical water splitting: 3D energy flow analysis of a volumetric fixed-bed reactor design. Int. Journal of Hydrogen energy, in press
9. Bulfin B, Lowe AJ, Keogh KA, Murphy BE, Lübben O, Krasnikov SA and Shvets IV. 2013. Analytical Model of CeO2 Oxidation and Reduction. The Journal of Physical Chemistry. 117(46):24129–24137.