

Hydrosol : Advanced monolithic reactors for hydrogen generation from solar water splitting

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Abstract - The HYDROSOL research team has developed an innovative solar thermo-chemical reactor for the production of hydrogen from water splitting, constructed from special refractory ceramic thin-wall, multi-channeled (honeycomb) monoliths that absorb solar radiation. The monolith channels are coated with active water-splitting materials capable to split water vapor passing through the reactor by 'trapping' its oxygen and leaving in the effluent gas stream as product pure hydrogen. In a next step, the oxygen 'trapping' material is solar-aided regenerated (i.e. releases the oxygen absorbed) and hence a cyclic operation is established. The first kind of such a pilot-scale reactor was designed, built and is currently operating in a continuous mode at a solar furnace facility, producing hydrogen by cyclic operation exclusively at the expense of solar energy; up to 40 cycles of constant H₂ production were operated in a row in a two-day continuous production of hydrogen. Further scale-up of the technology and its effective coupling with solar concentration systems are in progress to demonstrate large-scale feasibility of a 'solar hydrogen' production plant. Such plants can offer new opportunities to regions of the world that have a huge 'solar potential' like countries of Maghreb, that can become important local producers of 'clean hydrogen'.

Résumé - L'équipe de recherche de HYDROSOL a développé un réacteur thermochimique solaire innovateur pour la production de l'hydrogène par craquage de l'eau, réalisé à partir d'une paroi mince en céramique réfractaire spéciale, multicanaux de monolithes (en nid d'abeilles) qui absorbent le rayonnement solaire. Les canaux de monolithes sont enduits de matériaux actifs d'eau de craquage capables de craquer la vapeur d'eau passant par le réacteur 'en piégeant' son oxygène et en partant dans le jet de gaz résiduaire comme produit d'hydrogène pur. Dans une prochaine étape, le matériau de 'piégeage' de l'oxygène est régénéré à l'aide du solaire (c'est-à-dire libère l'oxygène absorbé) et par conséquent une opération cyclique est établie. Le premier genre de réacteur à l'échelle pilote a été conçu, et réalisé et fonctionne actuellement en mode continu dans des installations d'un four solaire, produisant l'hydrogène par opération cyclique exclusivement à l'aide de l'énergie solaire. Jusqu'à 40 cycles de production d'hydrogène constants ont été actionnés en une seule fois pour une production continue d'hydrogène de deux jours. D'autres mesures de développement de la technologie et son utilisation efficace avec les systèmes solaires de concentration sont en marche pour démontrer la faisabilité à grande échelle d'une usine 'd'hydrogène solaire'. De telles usines peuvent donner de nouvelles opportunités aux régions du monde qui ont 'un potentiel solaire' énorme comme les pays du Maghreb, ceux-là peuvent devenir des producteurs locaux importants de 'l'hydrogène propre'.

Key word: Hydrosol - Solar thermo-chemical reactor - Water splitting.

1. INTRODUCTION

The harnessing of the huge energy potential of solar radiation and its effective conversion to chemical fuels such as hydrogen is a subject of primary technological interest. One of the

reactions with tremendous economical impact because of the low value of its reactants is the dissociation of water (water splitting) to oxygen and hydrogen. The integration of solar energy concentration systems with systems capable to split water is of immense value and impact on the energetics and economics worldwide; by some is considered as the most important long-term goal in solar fuels production to cut hydrogen costs and ensure virtually zero CO₂ emissions. The current state of the art of solar chemistry for water splitting and hydrogen production is focused on the so-called redox pair cycles, based on redox materials that can act as effective water splitters at lower temperatures. According to this idea, in the first step (water-splitting) the activated redox reagent (usually the reduced state of a metal oxide) is oxidized by taking oxygen from water and producing hydrogen, according to reaction (1). During the second step the oxidized state of the reagent is reduced, to be used again (re-generation), delivering some of the oxygen of its lattice according to reaction (2):



Despite basic research with respect to active redox pairs (ferrites, iron oxide, manganese oxide, zinc oxide), solar reactor concepts have only recently been reported in the literature. Some are based on particles fed into rotating cavity reactors, concepts that are complicated and costly to operate and all employ dual reactor systems, one for the water-splitting and one for the regeneration process.

2. RESULTS - DISCUSSION

The uniqueness of the HYDROSOL approach is based on the combination of two novel concepts:

- nanoparticle materials with very high water-splitting activity and regenerability (synthesized by novel routes such as aerosol processes, combustion techniques and reactions under controlled oxygen pressure),
- their incorporation as coatings on special refractory ceramic monolithic reactors with high capacity for solar heat absorption.

Prior work of the Consortium members has demonstrated that multi-channeled honeycomb ceramics can act as solar heat collectors achieving temperatures in excess of 1100 °C; however the concept of combining them with high-temperature water-splitting materials for the exploitation of solar heat in the field of Solar Chemistry has never before been proposed. Through the HYDROSOL Project, the Consortium team has proposed and developed an innovative solar reactor for the production of hydrogen from the splitting of steam using solar energy (Fig. 1). The solar reactor is constructed from special refractory ceramic thin-wall, multi-channeled (honeycomb) monoliths optimized to absorb solar radiation and develop sufficiently high temperatures. The monolith channels are coated with an active water-splitting material, and the overall reactor looks very similar to the familiar catalytic converter of modern automobiles. When steam passes through the solar reactor, the active coating material splits water vapor by ‘trapping’ its oxygen and leaving in the effluent gas stream as product pure hydrogen (Fig. 2). In a subsequent step, the oxygen ‘trapping’ material is regenerated by increasing the amount of solar heat absorbed by the reactor (Fig. 3) and hence a cyclic operation is established. Highly active oxygen ‘trapping’/water-splitting materials (based on doped iron oxides) have been synthesized employing different techniques, the most active been produced by aerosol synthesis routes in APTL. The evaluation of the redox materials on the solar reactor proved the feasibility of solar hydrogen production by the HYDROSOL process and the stability of the redox/support assemblies.

Different approaches of a receiver-reactor for the continuous production of solar hydrogen have been set up and analyzed regarding capability for scale-up, thermal efficiency, technical

reliability, flexibility for modification and capability of pressurizing. The final decision was taken in favor of a modular arrangement including individual reaction chambers with fixed honeycomb absorbers. A fixed absorber avoids movable parts of the receiver as well as of devices for the drive of those movable parts. The modular set-up itself allows for a continuous provision of solar hydrogen, because one part of modules splits water while the rest is being regenerated. After completion of the reactions the regenerated modules are switched to the splitting process and vice versa by switching the feed gas. This general design concept has been transferred into a detailed design of the so-called 'conti reactor' (Fig. 4, 5). The approach resulted in an integrated solar receiver/reactor concept for the exploitation of solar heat that has never before been realized. The first kind of such a pilot-scale reactor was designed, built and is currently operating in a continuous mode at a solar furnace facility, producing hydrogen by cyclic operation exclusively at the expense of solar energy; up to 40 cycles of constant H_2 production were operated in a row in a two-day continuous production of hydrogen (Fig. 6).

This way of operation is transferable to a solar tower application in principle. In fact the HYDROSOL technology is the first demonstration of solar chemistry-based hydrogen production from water, with a future potential - when employed in combination with other solar thermal applications such as power plants - to achieve a hydrogen cost of 24 Eurocent/kWh in the medium-term and of 10 Eurocent/kWh in the long-term. Reactor efficiencies up to 28 % and process efficiencies of up to 9 % were found. Those figures are in a range typical for that size of a receiver-reactor. An increase of efficiency is expected by decreasing the amount of flushing gas, by enhancement of the illumination of the monolith, by using monoliths with larger depth, and in particular by scaling-up the reactor.



Fig. 1: Front view of the solar water-splitting receiver-reactor [1]

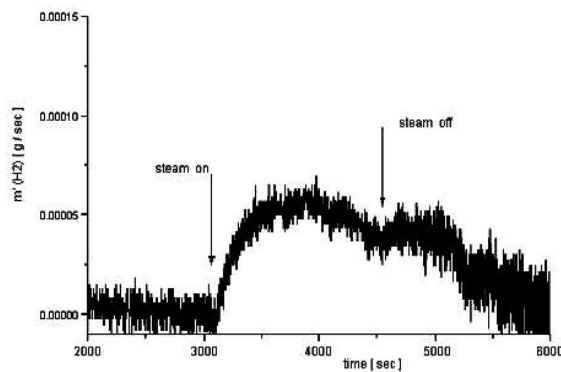


Fig. 2: Mass flow of hydrogen during splitting of water [2]

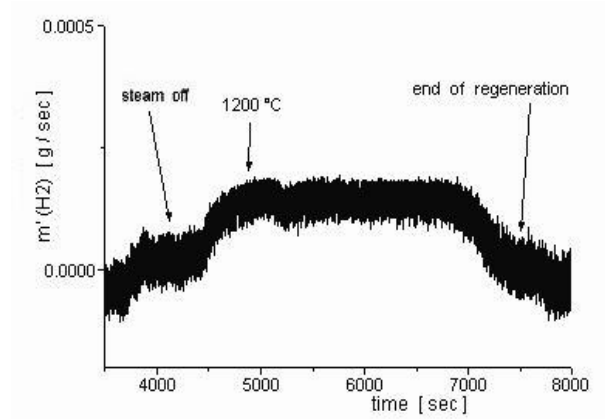


Fig. 3: Mass flow of oxygen during regeneration [2]

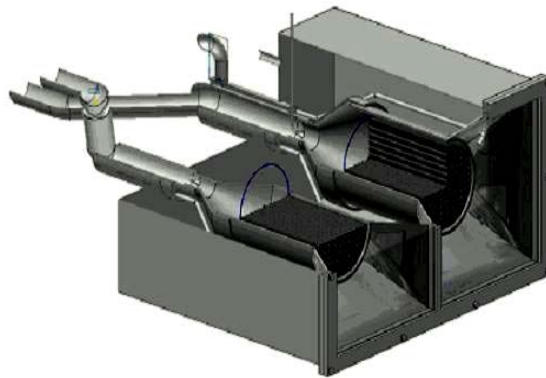


Fig. 4: schematic of two-chamber reactor ('conti reactor') for the continuous production of hydrogen [3]

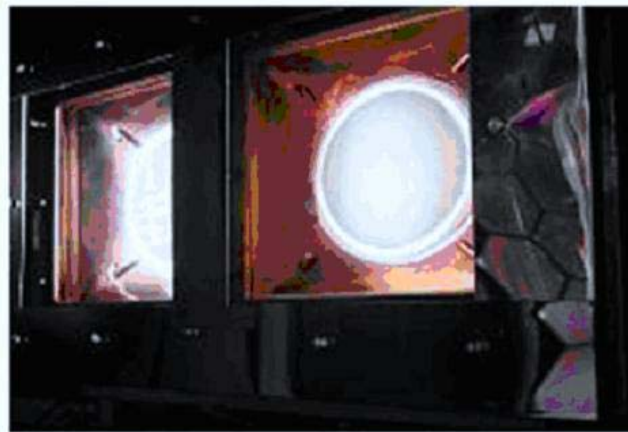


Fig. 5: actual reactor in operation [3]

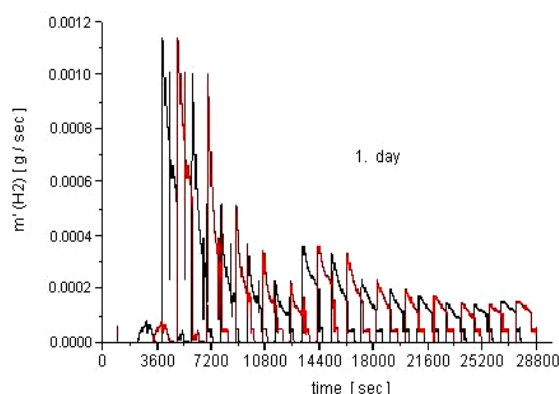


Fig. 6: Quasi-continuous production of hydrogen: mass flow of hydrogen during the first day of testing of two coated monoliths [3]

3. CONCLUSION

The developed technology not only produces hydrogen - a 'lean' fuel considered to be the energy source of the future with the advancement of fuel cell technology - but employs entirely renewable and abundant energy sources and raw materials - solar energy and water respectively - without any CO₂ emissions, in an entirely 'clean', natural and environmentally friendly way, addressing thus issues of universal concern and importance. Based on these results, current efforts involve further scale-up of the technology and its effective coupling with solar concentration systems like solar towers in order to demonstrate large-scale feasibility of a solar plant for the production of solar Hydrogen.

REFERENCES

- [1] C. Agrafiotis, M. Roeb, A.G. Konstandopoulos, L. Nalbandian, V.T. Zaspalis, C. Sattler, P. Stobbe and A.M. Steele, '*Solar Water Splitting for Hydrogen Production with Catalytic Monolithic Reactors*', Solar Energy, Vol. 79, N°4, pp. 409 - 421, 2005.
- [2] M. Roeb, C. Sattler, R. Klüser, N. Monnerie, L. de Oliveira, A.G. Konstandopoulos, C. Agrafiotis, V.T. Zaspalis, L. Nalbandian, P. Stobbe and A.M. Steele, '*Solar Hydrogen Production by a Two-Step Cycle Based on Mixed Iron Oxides*', Journal of Solar Energy Engineering - Transactions of the ASME, Vol. 128, pp. 125 - 133, 2006.
- [3] M. Roeb, N. Monnerie, M. Schmitz, C. Sattler, A. G. Konstandopoulos, C. Agrafiotis, V.T. Zaspalis, L. Nalbandian, A. Steele and P. Stobbe, '*Thermo-Chemical Production of Hydrogen from Water by Metal Oxides Fixed on Ceramic Substrates*', Proceedings of the 16th World Hydrogen Energy Conference, Lyon, France, 13-16 June, 2006.
- [4] C. Agrafiotis, C. Pagkoura, S. Lorentzou, J.C. Hoguet and A. G. Konstandopoulos, '*Material Technologies Developments for Solar Hydrogen*', Proceedings of the 16th World Hydrogen Energy Conference, Lyon, France, 13-16 June, 2006.

INTERNATIONAL RECOGNITION

HYDROSOL project is internationally recognised and has been awarded with some prestigious prizes:

- The 'Global-100 Eco Tech' prize from the international exhibition Expo 2005 in Aichi, Japan, which grants '...global environmental technologies that contribute significantly to the resolution of global environmental problems and to the creation of a sustainable future ...'.
- The 'IPHE 2006 Technical Achievement Award' from the IPHE (International Partnership for the Hydrogen Economy) which has been given during a ceremony at the World Hydrogen Energy Conference (WHEC 2006, Lyon, France, 13-16 June 2006). IPHE has recognised HYDROSOL as '... the only solar-thermo-chemical cycle which is operational, completely closed and capable of continuous production of hydrogen...'.