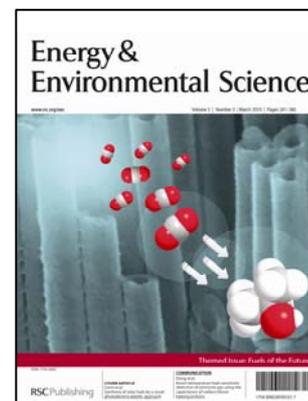


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Fuels of the Future

Guest Editors: Ben W.-L. Jang, Roger Gläser, Chang-jun Liu and Mingdong Dong



Editorial

Fuels of the Future

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Solar hydrogen: fuel of the near future

Mario Pagliaro,^{*a} Athanasios G. Konstandopoulos,^{*b} Rosaria Ciriminna^a and Giovanni Palmisano^a

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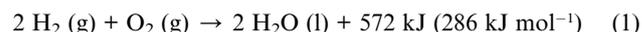
Renewable hydrogen produced using solar energy to split water is the energy fuel of the future. Accelerated innovation in both major domains of solar energy (photovoltaics and concentrated solar power) has resulted in the rapid fall of the solar electricity price, opening the route to a number of practical applications using solar H₂. Referring to several examples as well as to new technologies, this article provides insight into a crucial technology for our common future.

Introduction

Hydrogen generated by solar energy induced water splitting is the fuel, alternative to fossil fuels, capable of replacing fossil fuels and ultimately cease our dependence (or “addiction”,¹ to quote the former US president) on fossil oil and gas, abating the carbon dioxide emissions in the atmosphere causing global warming. Hydrogen gas has an enormous volume: 1 kg of H₂ at ambient temperature and atmospheric pressure has a volume of 11 m³ so that hydrogen storage basically implies a reduction in volume, generally accomplished by increased pressure (in gas cylinders with a maximum pressure of 80 MPa) or by lowering the temperature.²

In the last ten years, much hype has been associated with the hydrogen topic. Romm,³ for instance, has questioned the idea that hydrogen is an economically viable fuel for transportation because of the cost and greenhouse gases generated during production, the low energy content per volume and weight of the container, the cost of the fuel cells, and the cost of the infrastructure. Yet, the price of solar electricity in the last 3 years has fallen to such an extent, and the pace of innovation in both fields of solar energy has been so intense, that a number of unexpected practical applications have emerged that are indeed based to

solar hydrogen. In general, hydrogen cleanly reacts with oxygen in an highly exothermic reaction giving pure water as the unique exhaust by-product (eqn (1) and Fig. 1):



For practical reasons, fuel cells are usually operated with air rather than pure oxygen and low amounts of nitrogen oxides are formed among the actual exhaust products. PEM and SOFC (high temperature) fuel cells emit trace amounts of NO_x as shown by extensive tests at Georgetown University.[†]

Hydrogen must be generated by extracting it from hydrogen sources. Today most of the hydrogen we use comes from hydrocarbons which clearly contributes to the overall CO₂ emissions and thus to global warming. Once available, however, it is an excellent fuel that can replace hydrocarbons with numerous advantages, including a specific heat capacity 3 times higher than that of our best fossil fuel (natural gas, or methane). For example, in 2009, Italy's power company Enel started operating a 12 MW H₂-powered electricity plant in Venice's industrial zone of Porto Marghera, uniquely fuelled by hydrogen by-products from local petrochemical industries (Fig. 2). The turbines were specially designed to resist embrittlement from hydrogen, but in any case the only emission of hydrogen combustion is water.

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[†] <http://fuelcellbus.georgetown.edu/overview3.cfm>

Broader context

Renewable hydrogen produced using solar energy to split water is the energy fuel of the future. Accelerated innovation in both major domains of solar energy (photovoltaics and concentrated solar power) has resulted in the rapid fall of the solar electricity price, opening the route to a number of practical applications using solar H₂. New thermochemical water splitting using concentrated solar power (CSP) as well as CSP coupled to electrolysis has the potential to convert and store solar energy into clean hydrogen using a tiny fraction of the world's desert area to meet our present and future global energy needs. Photovoltaics, in turn, has the versatility required for supporting the creation of a distributed energy generation infrastructure in developing countries especially now that the price of PV solar electricity has fallen to unprecedented low levels. In all these cases, solar H₂ will be used to store energy and release it on demand either for fuel cells (to power homes and boats) or internal combustion engines and turbines (for powering cars, trucks and in thermoelectric power units). Referring to several examples as well as to new technologies, this article provides insight into a crucial technology for our common future.



Fig. 1 The only emission of Frauscher's Riviera 600 hydrogen-powered boat is clean water, whilst H₂ is cleanly obtained by photovoltaic electrolysis of water. (Photo courtesy of Fronius).



Fig. 2 First in the world to operate on such a scale, the 12 MW combined cycle plant in Venice's industrial zone of Porto Marghera fuelled by hydrogen by-products from local petrochemical industries. (Photo courtesy of Enel).

In contrast to fossil fuel deposits that are a concentrated source of high-quality energy, commonly extracted with power densities—of 10² or 10³ W m⁻² for coal or hydrocarbon fields, biomass energy production has densities well below 1 W m⁻², while densities of electricity produced by photovoltaic generation



Mario Pagliaro

Mario Pagliaro, a scholar at Italy's Research Council based in Palermo, is the founder and director of Sicily's Photovoltaics Research Pole. His research interests are in materials chemistry, solar energy, science methodology and management. Mario is the author of a large body of research papers and scientific books. His joint achievements include the commercialization of several new chemical technologies.



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Athanasios G. Konstandopoulos

Athanasios G. Konstandopoulos, founder and Director of APT Lab at CPERI/CERTH and a member of the faculty of Aristotle University of Thessaloniki, Greece, is the coordinator of the European "Hydrosol" projects. He is an expert in aerosol nanoparticle technologies and multifunctional structured reactors with applications in combustion engine emission control, solar hydrogen/fuels production and biotechnology.

He is the recipient of many awards, including the 2006 Descartes Prize of the European Commission.



Giovanni Palmisano

Giovanni Palmisano is a chemical engineer currently working on dye solar cells at Italy's CHOSE research center. He has co-authored 30 research papers on this and other chemistry and materials science topics. Giovanni is also an entrepreneur in the field of the solar energy business.

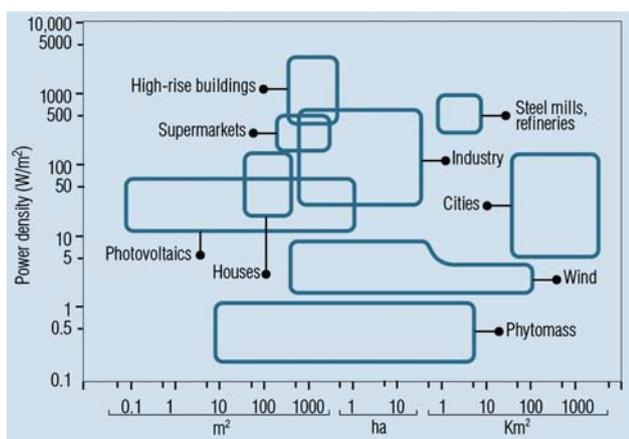


Fig. 3 Power densities for renewable fuels and energy consumers. Power density is the rate of energy production per unit of the earth's area, expressed in watts per square meter (W m^{-2}). (Reproduced from ref. 4, with permission).

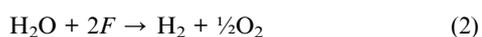
is around 20 W m^{-2} at peak power. Fig. 3 shows that the energy supply chain of today's fossil-fuelled civilisation works by producing fuels and thermal electricity with power densities that are one to three orders of magnitude higher than the common power densities with which our buildings and cities use commercial energies.⁴

Solar energy is the only renewable energy source with the versatility to meet both intensive production needs (through concentrated solar power, or CSP) and localized energy distribution demands (through onsite installed photovoltaic (PV) modules), whose price in the last 18 months has fallen by 75% (from 6 to less than 1.5 €/W).

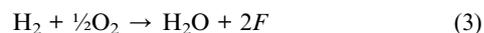
In the past three decades, computers and telephones have become decentralized and wireless. Solar energy will do the same for the energy industry. In other words, PV distributed on a small scale,⁵ instead of on today's industrial-size electricity grids, will begin to compete with the economies of scale that Edison's electricity transmission created over the last century. As the price of solar electricity approaches that of fossil energy, developing nations will adopt distributed solar generation as they did with mobile phones, jumping over fixed-line phones. Hence, in place of big fossil fuel power stations and a national electric grid, both fixed infrastructures with large costs, these nations will develop distributed generation.

Similarly, in wealthy nations where electricity costs are rapidly rising, citizens and companies can greatly benefit from solar energy, thanks to the now low upfront cost, and extremely low ongoing costs, and whose overall cost of finance amortized over the life of the equipment/capital investment vastly enhance the economics of solar energy.

In this context of rapid change, H_2 is an excellent storage option for storing the excess energy during the day for night time and cloudy days uses. Two complementary methods exist which rely on the two main solar energy technologies, namely photovoltaics (PV) and concentrated solar power (CSP). The first technology is water electrolysis using a photovoltaic current (eqn (2)):



where F is the Faraday constant measuring 1 mol of electricity (96 485 C). Once locally available, hydrogen can be used to generate electricity by the reverse of reaction 2:



which is the process that occurs in an $\text{H}_2\text{-O}_2$ fuel cell. Indeed, the same cell can work as a fuel cell or as an electrolyzer, depending on the operating conditions, which is not the case with other competing reactions for the production of H_2 . Overall, the process is able to locally create the required amount of hydrogen needed to power a house or a small boat's engine, such as in the case of the commercial electric boat powered by an $\text{H}_2\text{-O}_2$ fuel cell shown in Fig. 1.

Hydrogen can also be burnt in air within an internal combustion engine (ICE) such as in the case of the BMW Hydrogen 7 automobile equipped with a hydrogen tank. Like gasoline, hydrogen is highly flammable. Yet, Fig. 4 shows that due to the buoyancy of hydrogen (14.4 times lighter than air, rising at 20 m s^{-1} rate), the flame shoots up vertically, whereas gasoline is heavy and spreads beneath the vehicle.

The solar method to generate H_2 from water, better suited to addressing the energy-intensive needs of modern society, relies on CSP and is a catalytic thermochemical process that makes use of concentrated solar radiation to create a large surplus of hydrogen suitable for energy-intensive applications. Such solar technology not only produces hydrogen but employs entirely renewable and abundant *energy sources* and *raw materials*: solar energy and water, respectively, without any CO_2 emissions. Finally, one can use the CSP technology to produce large amounts of electricity and then store it as pure hydrogen through electrolysis. The convenience of this option will depend on the



Fig. 4 On the left is a vehicle with a hydrogen tank, and on the right a vehicle with a standard gasoline tank. Both tanks have been deliberately punctured and ignited. The top panel shows the two vehicles 3 s after ignition. The bottom panel shows the two vehicles 60 s after ignition. The hydrogen supply has burned off and the flame is diminished, whereas the gasoline fire has accelerated and has totally engulfed the vehicle on the right. (Photo courtesy of the University of Miami, reproduced from Physorg.com).

specific application. This article thus aims to provide insight into a crucial technology for our common future.

Water electrolysis

The splitting of water into gaseous H_2 and O_2 by the action of electricity is definitely an entirely clean process since no polluting by-products are formed provided that electricity is produced using either photovoltaics, hydroelectric, geothermal or aeolian power.⁶ In general, the product yield of reaction 2 is 100%, namely no electrical energy is wasted; and since the cost of water is negligible, eqn (2) shows that the entire economics of the process is driven by the cost of electricity. An electrolyte is dissolved in water to enhance conductivity and thus the overall rate of the process of water electrolysis.

In current commercial electrolyzers, the solution employed is a 30% KOH at 80 °C (alkaline electrolysis) and the electrolyte can be recovered and re-used. Alkaline electrolysis systems have efficiencies of 55–75% and make use of a ceramic microporous separator, whereas the electrodes are usually made of nickel, with the cathode coated in platinum and the anode coated in manganese oxide or tungsten oxide. Remarkably, the use of intermittent PV electricity results in two shortcomings: (i) its activity decreases with time, and (ii) shutdown of industrial cells provokes Ni dissolution at the cathode since this electrode is driven to more positive potentials by short-circuit with the anode. These shortcomings can be alleviated if Ni cathodes are *activated*, i.e. if they are coated with a thin layer of more active and more stable materials (Fig. 5).

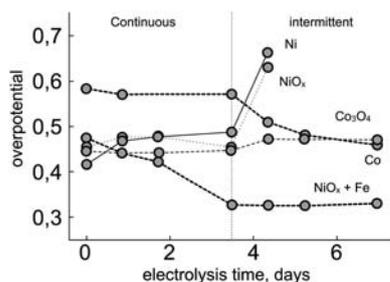


Fig. 5 Variation of overpotential (inversely proportional to activity) for O_2 evolution as a function of time for continuous and intermittent electrolysis. Under the latter conditions, Ni-based cathodes need protection by a thin layer of more active and more stable materials. (Reproduced from ref. 6, with permission).

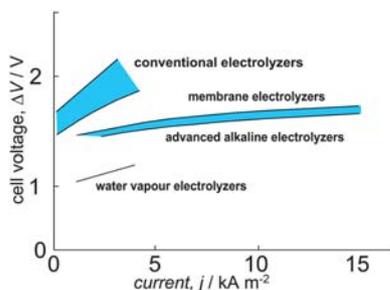


Fig. 6 Range of performance of different water electrolyzers. (Reproduced from ref. 6, with permission).

Table 1 Experimental parameters in alkaline electrolysis. (Reproduced from ref. 7).

$H_2O \rightarrow H_2 + \frac{1}{2}O_2$
Electrolyte: 25–30% KOH
$\Delta V = 1.65\text{--}2.00\text{ V}$, $j = 1\text{--}10\text{ kA m}^{-2}$
Energy consumption: 4–4.9 kW h m^{-3}
Current yield: 98–99.9%
H_2 purity: >99.8%

Fig. 6 shows that conventional (alkaline) electrolyzers show high overpotential and a relatively small production rate, whereas membrane and advanced alkaline electrolyzers display a very similar performance, with lower overpotential and much higher production rates.

Typically, a commercial alkaline electrolyzer produces H_2 by consuming 4.49 kW h m^{-3} of electricity with current yield and hydrogen purity both close to 100% (Table 1).⁷

In 2009 the Austrian companies Fronius, Bitter and Frauscher successfully presented Riviera 600: the first electric boat powered by solar hydrogen fuel cells. The concept is that of a self-contained energy supply provided by hydrogen simply obtained by photovoltaic electrolysis of water. The fuel cell makes it possible to use the solar power made available as H_2 when the (weather) conditions are optimal and to store the excess power so that it can be made available for later use as required. Extracted from water using photovoltaics and electrolysis, H_2 is oxidised in the fuel cell and the only emission is clean water (Fig. 1), completing a zero emission energy production cycle. The necessary investment for the hydrogen infrastructure gains more economic profitability with an increasing number of boats. The team “Future Project Hydrogen”⁸ has created budget calculations for the generation of hydrogen on site by use of photovoltaics under the premises of 10 boats for commercial use, for example, within a boat rental.

With a range of 80 kilometres with a full hydrogen tank and having been awarded a safety certificate by Germany’s TÜV, the boat is 6 m long, 2.2 m wide and weighs 1400 kg. Its 4 kW continuous power electric motor has twice the range of conventional battery-powered boats. The 47% efficiency of the noise-free fuel cell engine should be compared to the 18%–20%



Fig. 7 Re-fuelling of the 600 Riviera Frauscher boat is done in 5 min using a standard 350 bar filler coupling on the one hand plus a simple exchange of an empty cartridge for a full one on the other. (Reproduced from Frauscherboats.com, with permission).

efficiency of a conventional (steel) internal combustion engine. The main economic advantage compared with conventional electric boats is the fact that no time has to be spent charging the batteries. For conventional electric boats, 6–8 h of charging gives just 4–6 h of use. The hydrogen-powered electric boat requires only the time that it takes to change the cartridge: 5 min. The boat's fuelling system consists of a 20 kg cartridge that can be charged with up to 0.7 kg of hydrogen kept at 350 bar. Re-fuelling is done using a standard filler coupling on the one hand plus a simple exchange of an empty cartridge for a full one on the other (Fig. 7).

The energy filling ("Clean Power") station makes use of PV modules integrated in a 250 m² flat roof, and further connected to an electrolytic cell. Even at Austria's cold latitudes the station is capable of affording an annual yield of 823 kg hydrogen, equivalent to 1100 cartridges with a 27 200 kW h energy content, namely enough hydrogen to run a boat for 80 000 km. Its



Fig. 8 The Clean Power Station makes use of a 250 m² flat roof equipped with PV modules whose electric power output feeds an electrolyzer splitting water molecules. (Image courtesy of Fronius).

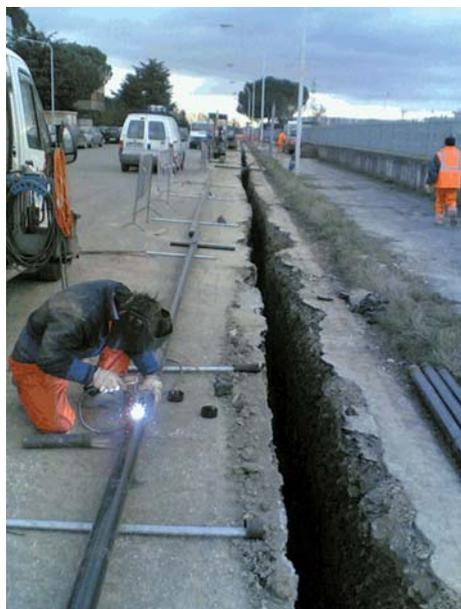


Fig. 9 Made of passivated steel and 1 km long, the first hydrogen pipeline in the world has been built in the Italian city of Arezzo and delivers pure H₂ at 3.5 bar to the fuel cells installed in 4 goldsmith companies. (Photo courtesy of La Fabbrica del Sole).

installation is simple thanks to the "container construction" design and can be carried out simply and quickly at many different locations. The station comprises electricity power charger, hydrogen and payment units (Fig. 8). For comparison, storing power in batteries over long periods of time is linked to huge losses due to self-discharge (5–10% per month), while the energy density is a fraction of that for hydrogen, which means that by storing energy in the summer in a battery of the same capacity, one would have no more energy available in winter.⁹

Another example that shows that photovoltaic renewable hydrogen is far from being solely a research topic is given by the world's first underground pipeline supplying H₂ to customers in the Italian city of Arezzo (Fig. 9).¹⁰ At present, the pipeline serves 4 companies and the HydroLAB with a main channel of around 600 m where the whole network is around 1 km.

Four goldsmith companies use it for industrial and energy needs *via* four 5 kW fuel cells and two 1 kW fuel cells at the HydroLAB, the laboratory for hydrogen and renewable energies (Fig. 10).¹¹

The aim was to set up a completely off-grid testing lab for technologies in the renewable energy sector, collecting data to test solar energy technologies linked with hydrogen production and use. Hence, solar panels provide electricity, solar thermal vacuum tube panels provide heat for room heating and feed a 5 kW solar cooling machine (Fig. 10) in order to get zero-emission air conditioning in summer. Waste water is completely



Fig. 10 The HydroLAB is completely off-grid since photovoltaic solar panels provide electricity and solar thermal vacuum tube panels provide heat for room heating and feed a solar cooling machine (5 kW, the smallest in Italy) in order to get air conditioning at zero emission in summer. (Photo courtesy of La Fabbrica del Sole).

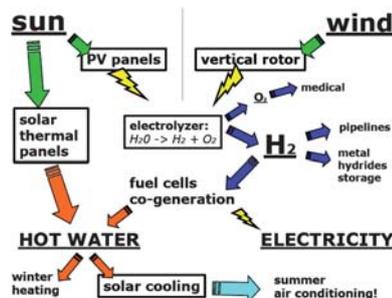


Fig. 11 Sun and wind provide all the energy needed to power the HydroLAB in Italy, and solar hydrogen is used to store the intermittent energetic supply of solar irradiation. (Image courtesy of La Fabbrica del Sole).

recycled through a fito remediation dry technique and rain is collected and stored (Fig. 11). The technologies implemented are continuously monitored, with the aim of further optimization in view of widespread commercial application in the building industry.

Today, when solar panels generate more electricity than a home is using, the excess is simply fed back into the grid, essentially subtracting from the homeowner's utility bill. In an off-grid application, the excess is put into batteries. But fuel cells are more versatile and their price is rapidly declining.

Existing electrolyzers are expensive. Hence, the challenge is devising a system that is efficient enough to make energy inexpensively. In general, however, PV electricity should be used as such, for electricity is the highest quality energy available; but this will require in its turn the introduction of new generation batteries able to recharge rapidly with large amounts of energy. Yet, the idea to use the PV energy to crack water molecules into hydrogen and oxygen and used later in a fuel cell to make electricity when the sun is not shining is general. The concept is a closed-loop system in which hydrogen oxidized with air in the fuel cell creates water, which is captured and used again.

A promising alternative process to split water into its elements is a based on a cobalt phosphate catalyst developed by Nocera and co-workers which can operate in plain water at atmospheric pressure mimicking photosynthesis.¹² The system makes use of a traditional anode (positively charged electrode in an electrolytic cell) consisting of indium tin oxide for the splitting of water by electrolysis upon which the "cobalt phosphate" solid catalyst is absorbed when current is passed through a solution containing Co^{2+} cations and HPO_4^{2-} anions. The catalyst forms *in situ* as the amount of charge passed during the course of an 8 h electrolysis far exceeds what could be accounted for by stoichiometric oxidation of the Co^{2+} in solution. The researchers, however, have worked only on one half of the problem (the anode) and at present this solution offers no alternative to the platinum-based cathode. A company (Sun Catalytics) was established to commercialize this new versatile, and affordable catalyst that splits water into oxygen and hydrogen fuel. Despite the advantages, water electrolysis and hydrogen/oxygen fuel cell technology still face challenges. For instance, the electrodes used in water electrolysis are currently coated with platinum, which is not a sustainable resource, and researchers are currently investigating the employment of nanomaterials with a large reduction on the amount of precious metal needed. Indeed, the main advantage of Nocera's catalyst that splits the water molecules using cobalt phosphate is that it is far cheaper and more abundant compared to expensive metals such as platinum.

Thermochemical water splitting

On the larger scale required to make solar-based H_2O splitting using only the energy of the sun a practical technology in terms of quantity and cost, the thermochemical redox-cycle process using a simple and robust materials is necessary, with manufacturability on a large scale at competitive costs developed in the context of the EU-funded Hydrosol project.¹³ The process—an endothermic reaction that requires an energy input—employs a multichannel ceramic honeycomb reactor resembling the familiar catalytic converter of automobiles, coated with active

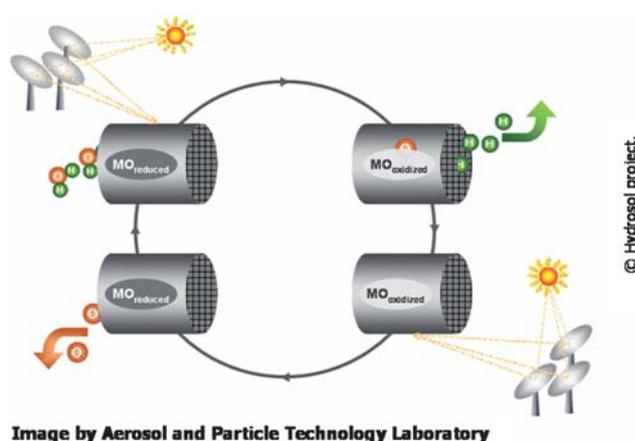
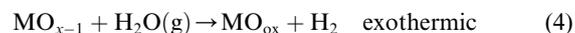


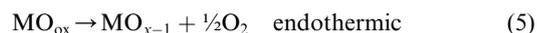
Image by Aerosol and Particle Technology Laboratory
Fig. 12 Scheme for the solar thermo-chemical water splitting cycle. (Reproduced from hydrosol-project.org, with permission).

water-splitting materials that are heated by concentrated solar radiation using a set of mirrors that is used to concentrate the solar energy, increasing the temperature in the reactor (Fig. 12).

In the first step of 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 (4):¹⁴



During the second step the oxidized state of the reagent is reduced, to be used again (regeneration), delivering some of the oxygen of its lattice according to reaction (5):



The advantage is the production of pure hydrogen and the removal of oxygen in separate steps, avoiding the need for high-temperature separation and the chance of explosive mixture formation. The active redox material is in fact capable of water-splitting and regeneration, so that complete operation (water-splitting and redox material regeneration) is achieved in a *closed* solar reactor.

The concept has been proven experimentally for pairs of oxides of multivalent metals or metal/metal oxide systems (for example, in the case of the highly promising ZnO/Zn system studied by Steinfeld and co-workers).¹⁵ However, even though water splitting is taking place at temperatures lower than 700°C , material regeneration (*i.e.* reduction) takes place at much higher temperatures ($>1600^\circ\text{C}$). In addition, despite basic research with respect to active redox pairs, solar reactors reported in the literature are based on particles fed into rotating cavity reactors, concepts that are complicated and costly to operate.

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 (synthesised by novel routes such as aerosol processes, combustion techniques and reactions under controlled oxygen pressure) and their incorporation as coatings on special refractory ceramic monolithic reactors whose geometry first emerged from traditional chemical engineering with its most familiar application to automobile catalytic converters. The solar thermo-chemical reactor for the production of hydrogen from water splitting is



Fig. 13 The monolith channels are coated with active water-splitting materials capable of splitting water vapor passing through the reactor by 'trapping' its oxygen and leaving hydrogen in the effluent gas stream as product pure. (Reproduced from hydrosol-project.org, with permission).

constructed from special refractory ceramic thin-wall, multi-channeled (honeycomb) monoliths (Fig. 13) that absorb solar radiation.

The reactor contains no moving parts, and with an overall efficiency of about 70%, the water vapour is cleanly converted into hydrogen.¹⁶ The hydrogen produced is indeed clean and ready for use. Multi-cyclic solar thermo-chemical splitting of water was successfully demonstrated on a pilot solar reactor (Fig. 14) achieving constant hydrogen production exclusively at the expense of solar energy. Single-phase doped spinel (A_xB_y)- Fe_zO_4 (where A and B denote the bivalent dopant metals Ni, Mn or Zn, obtained by aerosol spray pyrolysis of a solution of the metal precursor salts) exhibited both the highest water conversion and hydrogen yield, being capable of splitting water at relatively low temperatures (800 °C) with water conversions of up to 80% and hydrogen being the only reaction product.¹⁷

The first 100 kW/reactor continuous pilot plant scale was inaugurated on the Plataforma Solar de Almería, Spain, on March 31st 2008, being the first ever, closed solar-only, thermochemical cycle for hydrogen production. Up to 40 cycles of constant H_2 production were operated in a row in a two-day continuous production of hydrogen. Operation has demonstrated that the combination of CSP facilities coupled with high



Fig. 14 In March 2008, a 100 kilowatt reactor for producing hydrogen through water splitting using solar energy was put into commission at the Plataforma Solar in Almería as part of the Hydrosol project. The reactor is located inside the tower on the right. (Reproduced from hydrosol-project.org, with permission).

temperature processes will be a viable way to produce large amounts of hydrogen at a reasonable cost without any greenhouse gas emissions, paving the way for a purely renewable solar hydrogen economy. 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.¹⁸

Outlook and perspectives

In a recent perspective paper based on order of magnitude calculations,¹⁹ without referring to environmental arguments but focusing on economic convenience only, Abbott has suggested that sunlight is the scalable source of power on which our future energy needs must rely, based on low-tech CSP in place of photovoltaic electricity. Smil, on the other hand, suggests that even if a non-fossil world may be highly desirable, many decades will be needed for solar energy to capture substantial market shares on the global market, because of the enormity of requisite technical and infrastructural requirements. Yet, as Nocera puts it, the shift to a distributed power distribution infrastructure where each home can produce and store enough electricity from the sun to be self-sufficient (Fig. 15) is *necessary* because as billions of people in countries of Africa or of Asia start using higher amounts of energy compared to today's consumption, the world's energy needs will continue to explode in the coming years. H_2 is the fuel of the future because it solves the intermittency of supply of free solar energy, meeting one key requirement of modern societies: the continuous flows of energy. Of course, human activity and energy usage correlates significantly with the delivery of radiation from the sun, making solar hydrogen an excellent load-following clean technology.

A hydrogen economy makes sense, even if there are efficiency losses in liquefying and delivering H_2 ,²⁰ because the available

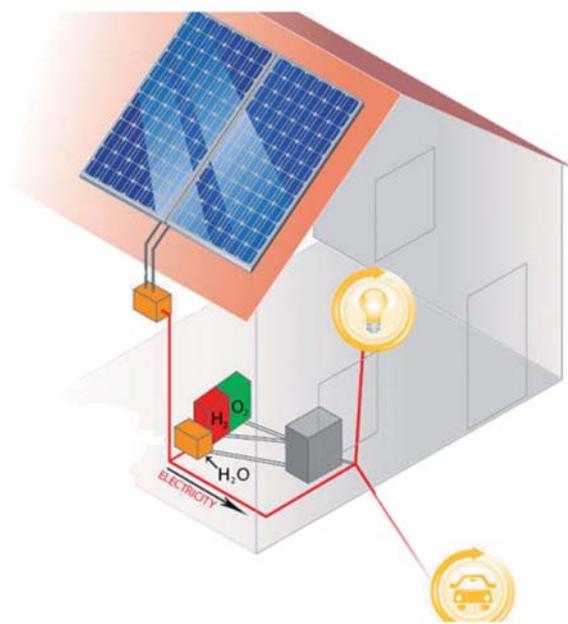


Fig. 15 During the day PV modules power the home. At the same time, excess energy is used to split water into H_2 and O_2 for storage and subsequent usage in fuel cells. (Adapted from MIT, with permission).

solar power is virtually unlimited and the collector technology is low-cost. As the sun delivers 5000 times our present global power needs, as little as a 500 by 500 km² area is needed to supply the world's energy needs (a tiny fraction of the world's desert area); using mirrors, focused sunlight can viably heat water for generating electricity *via* a conventional steam turbine. As put by Abbot:

“The point about solar energy is that there is so much of it that you only have to tap 5% of it at an efficiency as tiny as 1% and you already have energy over 5 times the whole world's present consumption... There is so much solar that all you have to do is invest in the non-recurring cost of more dishes to drive a solar-hydrogen economy at whatever efficiency it happens to sit at.”

For Abbott, pure H₂ (ready for combustion) should be preferred to both electric batteries and hydrogen fuel cells as the latter are not scalable due the use of expensive membrane technology as well as the expensive metal catalysts (platinum) or conducting metal ions (lithium), respectively.

With the same logic, solar energy concentration systems integrated with systems capable of *directly* splitting water will have an immense impact on energy economics, as they require no electrolysis to provide affordable, renewable solar hydrogen with virtually zero CO₂ emissions. 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.

The intrinsic versatility and the fall of the price of PV electricity supports the option to use solar PV stations to locally produce electricity as well as relatively small amounts of H₂ to power cars or boats powered by fuel cells. If a 250 m² solar station like the one shown in Fig. 8 in Austria can produce 823 kg of pure H₂ per year, in European regions like Sicily where PV electricity has already reached the grid-parity,²¹ this figure should be doubled at a fraction of the cost. Furthermore, new generation batteries and fuel cells will be nanotechnology-based,²² requiring ever less amounts of “exotic” metals and ensuring unprecedented performance in terms of power delivered or rate of charge.

But when will our global energy needs likely be met with the sun using solar farms distributed throughout the world?²³ Very shortly, we argue and namely within the next decade. And this is based on pure economic and national security reasons. What is, for example, the interest of a country like the US, the world's largest economy, to go ahead with a dependence on foreign oil when it owns huge deserts regions that are exceptionally suited to a massive adoption of solar energy?²⁴ Despite the 2008–2009 (and continuing) global economic recession in which the world's manufacturing output dropped by 30%, the price of oil remains >70 \$/barrel. This can only accelerate the transitions to solar energy as many countries have the urgent need to reduce the public debt that exploded following the public bailout of the financial system. Hence, they need to reduce the import of foreign oil and natural gas that even in a relatively small country like Italy costs 60 billion €/year. Similarly, other oil-free semidesertic countries such as Jordan, Israel or Morocco have no interest to continue their dependence on foreign fossil fuels. Indeed, all the latter countries have announced detailed plans for adoption of large-scale solar energy projects.

In Iceland, where abundant geothermal energy is freely available and the country is facing a most serious economic crisis, H₂ manufactured by water electrolysis is increasingly used to power private cars, public buses and boats with the aim of expanding its use in the large fishing fleet of the country.²⁵ And in Berlin there are two hydrogen filling stations open to the public. In general, the required infrastructure to support the use of hydrogen as a fuel will have to be developed.²⁶

Bettiol argues that renewable energy will be a local, hi-tech business with a global impact.²⁷ And it is remarkable to see how in practice this is occurring. For example, all three companies involved in the “Future Project Hydrogen” are based in Austria, very close to each other. Scientific and technical advice was provided by the Technical University of Graz, whereas the project was realized with support of the European Union regional programs and further funding from one of Austria's regions. The first 600 Riviera boat is commercialized at 150 000 €, with the first exemplars to be delivered to customers in early 2010.

As the number and reach of similar successful projects implemented worldwide grows, the huge potential of solar energy in both developing countries endowed with ample solar energy like China as well as in wealthy countries such as the US or Australia will become self-evident. We add to this our idea that further progress will increasingly make use of alternative forms of financing whose ethical core on financing socially and environmentally sound projects will naturally have a great impact on the solar energy business. This will further accelerate adoption of solar hydrogen and solar electricity until when solar energy will be the most economically and technically convenient option, replacing our dependency on fossil fuels.

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References

- 1 G. W. Bush, *State of the Union Address*, 2006, www.whitehouse.gov/stateoftheunion.
- 2 A. Züttel, Materials for Hydrogen Storage, in *Catalysis for Sustainable Energy Production*, ed. C. Bianchini and P. Barbaro, Wiley-VCH, Weinheim, 2009, pp. 235–269.
- 3 J. J. Romm, *The Hype about Hydrogen: Fact and Fiction in the Race to Save the Climate*, Island Press, Washington D. C., 2004.
- 4 V. Smil, 21st century energy: Some sobering thoughts, *OECD Observer*, 2006, **258/59**, 22.
- 5 T. Bradford, *Solar Revolution The Economic Transformation of the Global Energy Industry*, MIT Press, Boston, 2006.
- 6 E. Guerrini and S. Trasatti, Electrocatalysis in Water Electrolysis, in *Catalysis for Sustainable Energy Production*, ed. C. Bianchini and P. Barbaro, Wiley-VCH, Weinheim, 2009, pp. 235–269.
- 7 H. Wendt and G. Kreisa, *Electrochemical Engineering*, Springer, Berlin, 1999.
- 8 www.zukunftsprojektwasserstoff.at.
- 9 www.zukunftsprojektwasserstoff.at/typo/fileadmin/user_upload/download/FAQ_fuel_cell.pdf.

- 10 P. Fulini and E. Cecchini, *Hydrogen Project for Arezzo. Build up an underground hydrogen pipeline testing fuel cells in industrial areas. Hydrolab – The link between hydrogen and renewable energies*, World Hydrogen Technologies Convention, Montecatini Terme, Italy, 2007, <http://www.lafabbricadelsole.it/wp/wp-content/uploads/file/WHTC2007.pdf>.
- 11 www.idrogenoarezzo.it.
- 12 (a) M. W. Kanan and D. G. Nocera, *Science*, 2008, **321**, 1072; (b) M. W. Kanan, Y. Surendranath and D. G. Nocera, *Chem. Soc. Rev.*, 2009, **38**, 109.
- 13 Co-ordinated by the Greek Aerosol and Particle Technologies Laboratory, the consortium consisted of; the German Aerospace Centre, Stobbe Technical Ceramics from Denmark and Johnson Matthey Fuel Cells from the UK. www.hydrosol-project.org.
- 14 C. Agrafiotis, M. Roeb, A. G. Konstandopoulos, L. Nablondian, V. T. Zaspalis, C. Sattler, P. Stobbe and A. M. Steele, *Sol. Energy*, 2005, **79**, 409–421.
- 15 L. Schunk, P. Haeberling, S. Wepf, D. Wuillemin, A. Meier and A. Steinfeld, *J. Sol. Energy Eng.*, 2008, **130**, 021009.
- 16 http://ec.europa.eu/research/star/index_en.cfm?p=22_main.
- 17 C. C. Agrafiotis, C. Pagkoura, S. Lorentzou, M. Kostoglou and A. G. Konstandopoulos, *Catal. Today*, 2007, **127**, 265.
- 18 A. G. Konstandopoulos, Solar Hydrogen from Thermochemical Water-Splitting: The HYDROSOL process and beyond, in *The Fuel Cells and Hydrogen Joint Technology Initiative*, Stakeholders General Assembly, Brussels, 2009. <http://ec.europa.eu/research/fch/pdf/konstandopoulos.pdf#view=fit&pagemode=none>.
- 19 D. Abbott, *Proc. IEEE*, 2010, **98**, 42.
- 20 U. Bossel, *Proc. IEEE*, 2006, **94**, 1826. This paper does not consider the case of using sun to generate the hydrogen.
- 21 W. Hoffmann, president of the European Photovoltaic Industry Association, commenting the study *SET For 2020*, 2009. See also: <http://greeninc.blogs.nytimes.com/2009/06/22/industry-group-says-solar-to-become-cost-competitive-in-italy-next-year/>.
- 22 M. Pagliaro, *Nano-Age*, Wiley-VCH, Weinheim, 2010.
- 23 N. Armaroli and V. Balzani, *Angew. Chem., Int. Ed.*, 2007, **46**, 52.
- 24 This is the aim of the *Desertec* project first conceived in Germany and now being advanced by a consortium of German enterprises: <http://www.desertec.org>.
- 25 <http://www.newenergy.is>.
- 26 S. Pogutz, A. Russo and P. Migliavacca, *Innovation, Markets and Sustainable Energy: The Challenge of Hydrogen and Fuel Cell*, Edward Elgar, Cheltenham, 2009.
- 27 C. Bettioli, *Il Futuro, Seminar “Marcello Carapezza”*, CNR, Palermo, 2009.