

# Advanced Technologies for Green Hydrogen Production

Arturo de Risi , Gianpiero Colangelo  and Marco Milanese \*

Department of Engineering for Innovation, University of Salento, 73100 Lecce, Italy

\* Correspondence: marco.milanese@unisalento.it

Hydrogen represents a versatile fuel that has found usage in several sectors, such as automotive, aerospace, chemical industries, etc. Today, fossil fuels, due to their high hydrogen content, are the dominant source of hydrogen production and steam methane reforming is the most widely used technology: over 95% of the current production of hydrogen is based on the reforming of fossil fuels. However, in the near future, in order to reduce fossil CO<sub>2</sub> emissions, hydrogen production is expected to gradually shift toward green solutions.

In this Special Issue entitled “Advanced Technologies for Green Hydrogen Production”, we analyze 14 contributions from different research areas, ranging from the photo-electrocatalytic process, to high-temperature water splitting, to photocatalytic water splitting, to biological hydrogen generation, to photo-electrocatalytic process, to green hydrogen integration with natural gas networks, power distribution networks, and chemical industry.

A brief summary of the content associated with each of the selected papers belonging to this Special Issue is presented below.

Currently, water electrolysis represents about 4% of the H<sub>2</sub> production, but at the state of the art, one of the main obstacles to the penetration of this technology is the low efficiency of the process. A valuable alternative is the photo-electrocatalysis, which is a powerful method utilizing solar energy to provide the required thermodynamic potential of 1.23 V needed for the splitting of water and producing hydrogen [1,2]. This way, solar energy can be stored as chemical energy in hydrogen and is thus an alternative energy harvesting and storage technology.

Another carbon-free technology for hydrogen production is based on the thermal water splitting process. It has been extensively investigated as a promising and effective approach for hydrogen production, but the main obstacle to its industrialization is the elevated reaction temperatures, up to 2500 °C.

Borretti [3] described the thermochemical water splitting cycles capable to produce hydrogen with high-temperature concentrated solar energy at temperatures of 1000 to 1100 °C. Its work showed that three-step cycles offer the best compromise between the typical working temperature of concentrated solar energy systems, reduced complexity, and higher level of technological readiness, among the available options. In fact, two steps cycles require too much higher temperatures, while four steps cycles, although can work with lower temperatures, are quite complex.

In order to reduce the working temperature of thermochemical water splitting cycles, Sadeghi and Ghandehariun [4] studied an integrated standalone solar thermochemical hydrogen production system based on carbonate molten salt. Particularly, they developed a dynamic analysis of a system, including a solar power tower based on (LiNaK)<sub>2</sub>CO<sub>3</sub> as heat transfer fluid, a supercritical Rankine cycle, and a four-step thermochemical Cu–Cl cycle. The proposed system was investigated from a thermodynamic and economic point of view by means of the total revenue requirement method. Based on the multi-objective optimization procedure, the main outcomes of this study were that the optimal system design had an overall thermal efficiency and levelized cost of hydrogen of 29.18% and \$7.58/kg H<sub>2</sub>, respectively.



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An alternative way to produce hydrogen with clean and low-cost solar energy is represented by photocatalytic water splitting. Especially semiconductor photocatalysts, with suitable band gaps and high solar efficiency, have been reported by lots of literatures, such as  $\text{TiO}_2$ ,  $\text{SnO}_2$ ,  $\text{Fe}_2\text{O}_3$  or  $\text{CeO}_2$ , etc. For example, Pan et al. [5] prepared and tested nickel-cobalt bimetal sulfide synergistic modified CdS nanorods with active facets. Particularly, they evaluated the photocatalytic performance of CdS/Ni-Co-S, finding a remarkable HER performance and stability.

The biological hydrogen generation process also can play an important role in  $\text{H}_2$  generation due to its features, such as versatile feedstock (lignocellulose, organic waste, and wastewater) and no green-house gas emissions.

Fakhrulrezza et al. [6] proposed a dynamic simulation model, based on an existing experimental design setup, that uses a one-dimensional heat-transfer analysis method to simulate a biohydrogen production system coupled with an integrated gasification combined cycle power plant. The results showed a significant decrease in the starting time of the biohydrogen production process.

Pajak et al. [7] presented a study on a biogas reforming reactor aimed to optimize its temperature distribution by means of a novel arrangement of catalysts. Their results confirmed a significant enhancement of reaction effectiveness, due to the better thermal conditions, giving a valid strategy for increasing the biogas reforming efficiency.

Sanchez et al. [8] studied the biomass potential for producing power via green hydrogen. They analyzed a complex process based on several steps: biomass fermentation, bioethanol purification,  $\text{H}_2$  production via ethanol steam reforming (ESR), syngas cleaning by a CO-removal reactor, and power production in a high-temperature proton exchange membrane fuel cell (HT-PEMFC). The results demonstrated that the greatest effects on the power production, energy consumption, and process efficiency were steam-to-ethanol ratio used in the ESR, ethanol concentration in the raw bioethanol obtained after fermentation, and ESR temperature. Therefore, this study provided initial insight into the possibility of selecting suitable conditions for energy and green  $\text{H}_2$  production via ESR for a wide variety of bioethanol sources.

New technologies for biodigestion of food waste were studied by Tashyrev et al. [9]. Particularly, they analyzed a system based on a combination of aerobic and anaerobic microorganisms, algae, protozoa, aquatic micro- and macroinvertebrates, and fish to recycle multicomponent food waste and efficiently generate biohydrogen and biomethane. The proposed technology, relying solely on biological processes and requiring no chemicals or physicochemical methods, significantly reduces operating costs.

The exploitation of green hydrogen in the Italian natural gas network has been evaluated by Pellegrini et al. [10]. In their work, they analyzed the possibility of using the excess of electric energy produced by renewable energy power plants (RES) to feed electrolyzers for hydrogen production to be injected into the national natural gas (methane) pipeline network. The strategy of mixing green hydrogen with methane in a low percentage (less than 10%) has multiple advantages from economic, social, and environmental points of view, even if it still presents many legislative obstacles and technological issues to fix. Their work shows that currently up to 8100 ton/year of green hydrogen blending could be directly injected into the existing Italian natural gas pipeline which corresponds to an installed capacity of about 78 MW of electrolyzers with 488 M€ of capital cost.

Frankowska et al. [11] in their paper investigated a theoretical multi-criteria 2-D model of a system architecture to stabilize the operation of power distribution networks based on a hydrogen energy buffer. The importance of this work is related to the fact that there are still few studies about hydrogen supply chains with the functioning of electrical power grids. They developed a model that involves 49 variables in a 2-D system architecture covering the phases of the hydrogen supply chain (feedstock, production with storage, and distribution) in 4 groups of factors (technical, economic-logistical, locational, and formal-legal factors). The model considered the hydrogen utilities: conversion of electricity

to hydrogen, fuel cells converting hydrogen to electricity, hydrogen storage, and hydrogen utility application.

The green hydrogen in refueling stations is the main topic of the paper of Kavadias et al. [12]. In their work, they elaborated a design of the equipment and economic analysis of a hydrogen refueling system supplied with the hydrogen yielded by electrolysis with the electricity produced by a 10 MW wind plant. They elaborated on an optimization of the system taking into account different scenarios, operating conditions, and variables. In particular, they investigated the effects of the number of refueled vehicles on the return on the investment and the fuel cost in remote regions. Their results showed that a wind plant could be a good solution to produce hydrogen with the excess of yielded electricity. They concluded that in the case of low fuel cell electric vehicles penetration, the payback period presented significantly high values.

Green hydrogen can play a strategic role also for the decarbonization of heavy industries and in particular of chemical industries, as described in the work by Ostadi et al. [13]. They showed how a fully integrated electrolysis system in the chemical industry helps the decarbonization of the processes through the integration of RES. In particular, they concluded that the new process uses intermittent RES for CO<sub>2</sub> conversion to fuels (synthetic fuels, methanol, methane), enabling thermal integration, H<sub>2</sub> and O<sub>2</sub> utilization, and sub-process optimization for economic convenience. They showed how the new processes are able to reduce CO<sub>2</sub> emission for different applications: ferric iron reduction, municipal waste incineration, biomass gasification, fermentation, pulp production, biogas upgrading, and calcination.

The actual market conditions and the economic convenience of the production of green hydrogen have been studied by Jovan and Dolanc [14]. They used an electric hydropower plant in Slovenia to assess the feasibility of green hydrogen production. They analyzed the current prices and costs to compare different production techniques in order to obtain a realistic conclusion considering hydrogen a sustainable energy vector in industry, heating, transport, and the electricity production sectors. They concluded that green hydrogen could be competitive compared to traditional fuels in the transport sector with a proper policy of incentives.

The scientific works on advanced green hydrogen production technologies are many, from high-temperature water splitting, to photocatalytic water splitting, to biological hydrogen generation, but there is a lot of room to explore many scientific aspects that still do not have a clear theoretical and experimental answer.

**Conflicts of Interest:** The authors declare no conflict of interest.

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