

H₂ PRODUCTION BY WATER PHOTO-ELECTROLYSIS BY USING A NOVEL TiO₂ NANOTUBE ARRAY-BASED PHOTO-REACTOR

Claudio Ampelli*, Rosalba Passalacqua, Siglinda Perathoner, Gabriele Centi

Department of Industrial Chemistry and Material Engineering, University of Messina
Viale Ferdinando Stagno d'Alcontres, 31 - I-98166 Messina (ITALY)
* ampellic@unime.it

In this work we report on the use of a modular photoelectrochemical (PEC) device for the solar production of H₂ by water photo-electrolysis. The aim of the study was to obtain the maximum benefit from the solar irradiation, simulated by a Xe-arc lamp, through i) the development of novel nano-engineered photoactive materials, such as TiO₂ nanotube arrays prepared by anodic oxidation of Ti foils and ii) the correct design of the photo-reactor, which must have the best configuration to maximize the efficiency of the process. The presence of two distinct reaction chambers in our PEC system, allowed to form O₂ and H₂ as two separate gaseous streams, so limiting charge recombination phenomena and avoiding the fast back-reaction to water. Results in terms of H₂ production and generated photo-current showed Pt-doped TiO₂ nanotubes to be the best photocatalysts used, where their performances depended upon the operating conditions of the process (liquid or gaseous phase) and also on the parameters chosen during the synthesis of the samples (voltage, time of anodization and nature of the electrolyte).

1. INTRODUCTION

The environmental impact of human activities and the growing energy demand have accelerated the need to develop clean and safe energy conversion technologies and more effective processes to sustain the present level of development respecting the local and global environmental protection measures. There is the need on a short-term of new technologies for energy saving and efficiency, and use of biomass. On a medium term, a more rational use of renewable resources is needed, including solving the issue of energy storage and transport, and find a sustainable solution to CO₂ emissions, because the full transition to non-fossil fuels will require longer time. Finally, in a long-term, the renewable energy scenario, based in particular on solar energy, will become predominant (Centi et al., 2011).

Hydrogen represents a controversial point in the future energy system: there is a considerable interest on its use as energy vector and it can also be considered as a sustainable energy solution if it is produced from renewable resources (such as water and solar light), thus reducing the use of fossil fuels currently necessary for its production (Bockris, 2008). The conversion of solar energy into H₂ via water splitting process, in fact, is one of the most attractive ways to obtain clean and renewable energy. The main work in photochemical water splitting, at present, concerns the increase of the efficiency and stability of the photoactive materials, in the way to achieve the required efficiency benchmark of 10% that will be viable for commercial implementation. In order to perform this aim, two parallel lines of research have been pursued: the former refers to the synthesis of new materials with characteristics suited to be used as photo-catalysts (band gap near to the visible region, stability, non-toxicity, low cost etc.) (Mor et al., 2006); the latter is the correct evaluation of the engineering aspects concerning the photochemical reactor, to achieve an improvement of the process efficiency (irradiation pattern, geometrical configuration, material of construction, heat exchange, and mixing and flow characteristics) (Ampelli et al., 2009).

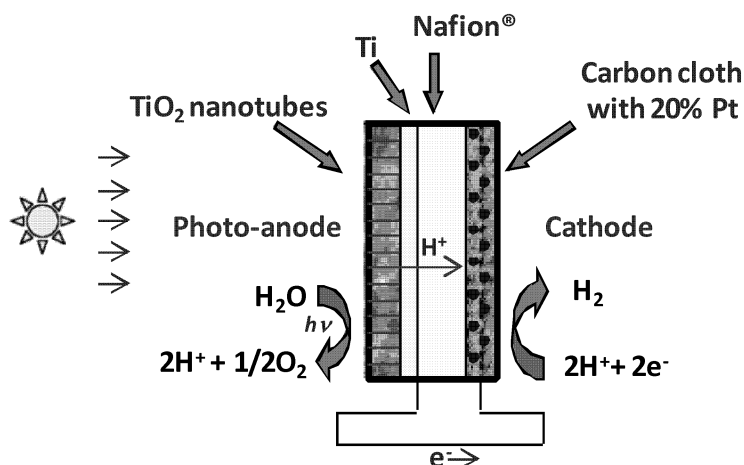


Fig. 1: Scheme of the Membrane Electrode Assembly (MEA) for the water photo-electrolysis.

In this work we report on the realization and development of an innovative photoelectrochemical (PEC) cell based on the use of TiO₂ nano-engineered array thin film as photo-anode for water splitting and/or ethanol photoreforming processes. The photo-reactor, built in Plexiglas and equipped with a quartz window, was realized in a highly compact configuration in order to reduce light scattering phenomena due to the water and maximize the photocatalytic efficiency (Ampelli et al., 2011b). The separation of the photo-induced process in two physically distinct areas related to water oxidation (to form O₂, protons and electrons) and proton reduction (to form H₂) shows many potential advantages, by limiting charge recombination and avoiding the fast back-reaction to water (Matsuoka et al., 2007). For a practical use of the PEC solar cell, its design is quite different from that commonly used in literature: the electrodes are in the form of a Membrane Electrode Assembly (MEA), taking advantage from the fuel cell technology: the anode and cathode films are separated from a proton-conducting membrane and deposited over a porous conductive substrate, which allows the efficient collection/transport of the electrons over the entire film, as well as the diffusion of protons to/from the membrane and an efficient evolution of the gases (Ampelli et al., 2010). The particular configuration of the PEC cell allows also to measure in-situ the photocurrent generated between the electrodes. In Fig. 1 a scheme of the MEA for the water photo-electrolysis is depicted.

This device could also be used to produce renewable H₂ by photocatalytic reforming of chemicals present in waste streams from agro-food or agro-chemical production, such as diluted streams of ethanol, glycerol, etc. There are many diluted waste streams containing ethanol and other organics, which are too diluted to be used as feed to make (i) H₂ by catalytic routes, (ii) methane by anaerobic digestion or (iii) in new generation fuel cells (Centi and van Santen, 2007). The photoreforming of these waste streams to produce H₂ is thus attracting.

2. PHOTO-REACTORS

The design of a photo-reactor is based on a careful evaluation of the factors which can influence the reactor performance: light source, geometrical configuration, material of construction, heat exchange and mixing and flow characteristics (Yue, 1985).

The irradiation source determines the range of wavelengths of the radiation in the electromagnetic spectrum. The choice of the most suitable lamp can be made by evaluating the reaction energy requirement with respect the specification of the lamps. If solar energy use is being considered, it should be noticed that the ultraviolet percentage in sunlight is quite limited (<4%). Moreover the light source must be mounted within a glass sheath or some suitable optical assembly to give a certain pattern of irradiation.

In choosing the reactor geometrical configuration it is necessary to determine the optical path of the light within the reactor, in a way to attain the maximum benefit from the pattern of irradiation and a good absorption of light photons. In conventional reactors the conversion for a given reactor volume is independent of geometry, if the effects due to flow characteristics are neglected. However, for photo-reactors, reactor geometry and the spatial relation between reactor and light source are vitally important. The three most commonly used geometries are: cylindrical, parallel and annular. In all the cases the irradiation occurs normal to the reactor surface.

The choice of material of construction for photo-reactors is severely limited by the requirement of light transmission. The choice of the designer is usually limited to different types of glass: optical glass, Pyrex glass, Vycor glass and quartz. The last generally gives the best performance in terms of light transmission, but is the most expensive. At short wavelengths, under 300 nm, quartz is the only appropriate material. The thickness of the reactor wall also diminishes the light transmission; this fact limits both the size of the reactor and the range of operating temperature and pressure.

Heat exchange is another important factor to take into account, especially in gas-solid systems. Since glass has low thermal conductivity, suitable devices must be designed to remove the heat generated by the lamp.

Mixing and flow characteristics must be carefully considered; they strongly depend on the phases involved in the process. For heterogeneous photo-reactions, contact between reactants, photons and catalysts must be facilitated, for example with agitation of the reacting mixture by means of a stirrer, in a way to attain a high degree of back-mixing (Cassano et al., 2005).

3. EXPERIMENTAL

3.1 Preparation of the photocatalyst

Nano-structured TiO₂ thin films were prepared by anodizing Ti foils (Alfa Aesar, 30 x 40 mm, 0.025 mm of thickness and 99.5% of purity). The method is useful to produce dense arrays of TiO₂ nanotubes, which grow by organizing themselves under an applied electric field (20-60 V). The mechanism is essentially based on the equilibrium between two reactions: the anodic growth of an oxide layer on the Ti metal surface and the simultaneous chemical dissolution of the oxide in presence of fluoride ions (or other complexing agents). The electrolyte used for the anodic oxidation is ethylene glycol with 2 vol. % H₂O and 0.3 wt. % NH₄F. Further details about the anodization conditions and geometry of the cell were reported elsewhere (Centi et al., 2007). The main advantage of this particular technique of preparation is the high grade of control on the nano-architecture, simply by adjusting some synthesis parameters, such as the electrolyte type, applied voltage, pH and anodization procedure, and it can also be easily scalable to large films (up to 20x20 cm) (Ampelli et al, 2008). Atomic Absorption Spectroscopy (AAS) and X-ray Fluorescence (XRF) were also used to check the purity of the solutions and analyze the amount of Ti dissolved in solution after the anodization. The nanostructured samples become crystalline after annealing at 450°C in air for 6 h with heating and cooling rates of 2°C/min.

3.2 Apparatus with photo-reactor

The apparatus for the photo-catalytic experiments mainly consists of: a solar illuminator source and a photo-reactor (Fig. 2). The lamp housing is furnished with: a Xe-arc lamp (ORIEL, 300 W), a set of lenses for light collection and focusing, and a water filter to eliminate the infrared radiation. The PEC reactor, made of Plexiglas and equipped with a quartz window, is homemade. It has a two-electrode configuration with two compartments for separated evolution of H₂ and O₂. The irradiated area is 5.7 cm². The photoanode is the nanostructured TiO₂ thin film supported over the porous Ti foil. The cathode is a carbon cloth (CC) loaded with Pt. The two electrodes are joint together by a Nafion[®] membrane. 1 M NaOH and 0.5 M H₂SO₄ aqueous solutions were used as electrolytes in the anodic and cathodic compartments respectively. Each solution circulates continuously between the solar cell and an outer reservoir.

The simplified process is as follows: (1) light crosses the quartz window and reaches the nanostructured film (photoanode) where photo-generated electron and hole pairs are generated and O₂ evolves, (2) protons pass through the Nafion[®] membrane, while electrons are collected and reach the cathode through an external wire, and (3) protons recombine with electrons, over Pt nanoparticles supported on CC, to give H₂.

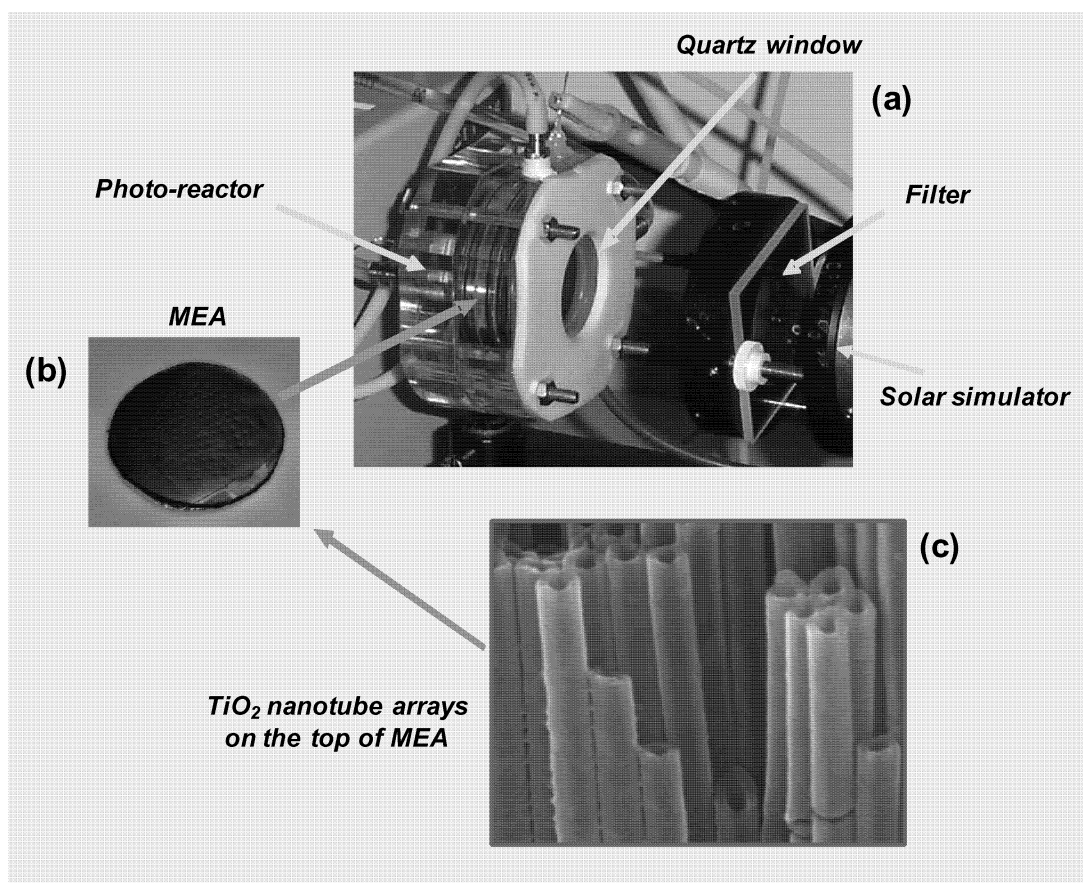


Fig. 2: (a) View of the lab-scale PEC photo-reactor; (b) image of the Membrane Electrode Assembly (MEA) and (c) SEM image of TiO_2 vertically-oriented nanotube arrays.

A potentiostat–galvanostat (AMEL 2049) was used to measure the generated photocurrent. H_2 and O_2 amounts in the gas streams were periodically determined with an on-line gas-chromatograph (GC), equipped with a molecular sieve 5A column and a thermal conductivity detector (TCD).

As already mentioned in the introduction, aqueous solutions of hydrolysis products of lignocellulose or waste solutions from biomass fermentation (e.g. diluted solutions containing bioethanol) can also be used to enhance H_2 formation by photoreforming. For this reason, ethanol was used as model reactant in some testing experiments.

4. RESULTS AND DISCUSSION

The conversion of solar energy into H_2 via water splitting process is one of the most attractive ways to obtain clean and renewable energy. The process needs to be furnished with solar energy: the photons must have the right energy to cover the band gap of the material used in order to allow the electrons to jump from the valence to conduction band and create a charge separation, with a lifetime long enough to be transformed into chemical energy. A band gap lower than 3.2 eV would be desirable since the visible region is the most part of solar spectrum and now the main efforts of scientists are turned to reduce the band gap of TiO_2 and/or to synthesize new materials with improved characteristics suited to be used as photo-catalysts. The decoration of the photo-substrate surface with metal nanoparticles facilitates the H_2 production as they work as electron attractor catalytic sites. From this point of view it is more correct to define the process as water photo-electrolysis instead

of water splitting: the oxidation of water to generate O_2 occurs on the TiO_2 surface in correspondence with the electronic holes (h^+) where water is absorbed (this location on the photo-catalytic surface acts as a photo-anode); the electrons created by the charge separation induced by solar light are strongly attracted by the metal nanoparticles, where they may combine with protons which are absorbed from the solution (the metal nanoparticles can be considered as cathodic centres). Unfortunately the back-reaction of recombination between H_2 and O_2 to form again water is favoured both thermodynamically and kinetically on the same catalysts used for its dissociation. That limits strongly the efficiency of process if only a compartment of reaction is used. The separation of the environment for the two semi-reactions in a PEC-type reactor may avoid the fast back-reaction since H_2 and O_2 streams are generated from different sides and they do not come in contact each to other. In this case the metal nanoparticles must not necessarily be deposited on TiO_2 photoanode (though they could improve the light absorption in the visible region), because the H_2 generation occurs on the other side of the PEC cell. The photoanode in a PEC solar cell, as introduced above, should be in the form of a porous thin film allowing a good light harvesting, fast transport of the protons and electrons produced during the water oxidation, and good contact with both the electron-collector substrate and proton-conductor membrane. The use of a specific nanostructure in the photoanode may improve the light harvesting and limit charge recombination at the grain boundaries with respect to an assembly of nanoparticles, while maintaining a high geometrical surface area necessary to improve the photoresponse. Anodic oxidation of Ti foils proved to be the most suitable preparation method to produce the photoanode, because it (i) can be cost-effective, (ii) allows a good control of the nanostructure in terms of 1D-array characteristics, vertical alignment, density and thickness, and (iii) can be easy scalable to large films. The nanostructured titania thin films may be used in either liquid or gas phase, particularly for the case of H_2 production by photoreforming. In order to understand better the importance to have a specific nanostructure in the photoanode, a comparison of the performances in terms of H_2 production by using different kinds of TiO_2 thin films was done in Table 1.

Table 1: Hydrogen evolution rate for different kinds of TiO_2 samples during water photo-electrolysis

	TiO_2 sample	Hydrogen ($mmol\ h^{-1}\ g^{-1}$)
<i>slurry</i>	P25 Degussa powder	0.227
	pressed powder (P25 Degussa) layer on Ti	0.473
<i>film</i>	TiO_2 nanotube array on Ti by anodization	3.200
	dense layer by sol-gel (dip-coating)	0.367

The most simple TiO_2 thin layer to be used as photoanode can easily be prepared by pressing commercial P25 Degussa TiO_2 on a conductive substrate. We used Ti foils as conductive substrate thus to make comparable this sample with nanostructured TiO_2 thin films prepared by anodic oxidation, described in the experimental part. Particular attention must be taken in casting the powder on Ti surface in order to avoid the detachment of the oxide layer during the tests in the solar PEC cell. There are several methods in literature to cast Degussa-type powders on conductive glass, but the best method which can be adapted for Ti foils seems to be the Doctor Blade technique. This is the best way to obtain a homogeneous layer in terms of thickness (Mills et al., 2003). During water photo-electrolysis process in the solar PEC cell, P25 Degussa TiO_2/Ti sample showed a H_2 evolution of $473\ \mu mol\ h^{-1}\ g^{-1}$. This value is about two times higher with respect to H_2 evolution obtained with the same powder in suspension by using a slurry-type well-mixed photoreactor ($227\ \mu mol\ h^{-1}\ g^{-1}$). This reactor has a quartz window with the same opening of the PEC cell and it is irradiated with the same solar illuminator; so results are well comparable. The increase of H_2 production is due to the reduced light scattering phenomena when P25 Degussa TiO_2 is used as a compacted thin film.

Another conventional method for preparing TiO_2 thin films is the sol-gel dip-coating technique. In this case H_2 production by water photoelectrolysis was quite similar to that of P25 Degussa TiO_2 ($367\ \mu mol\ h^{-1}\ g^{-1}$).

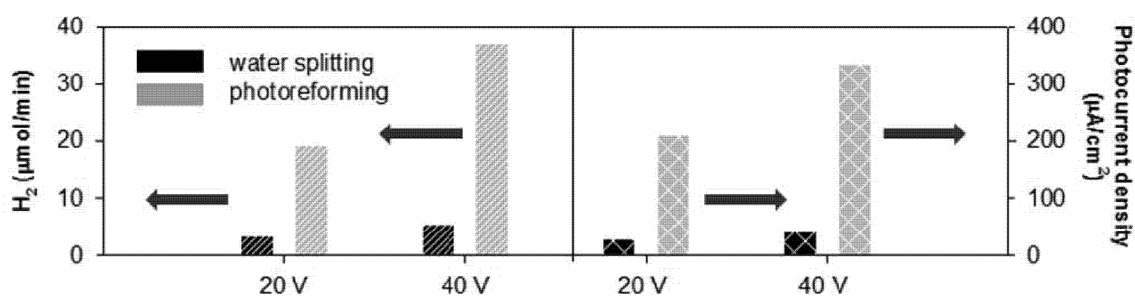


Fig. 3: Hydrogen evolution rate and photo-generated current during water photo-electrolysis and 10 vol.% ethanol photoreforming for samples anodized at different voltages.

The slightly worse performances could be attributed to the presence of ~15% rutile together with anatase phase in P25 Degussa TiO₂, while only anatase is present in the sample prepared by sol-gel method. The presence of a rutile/anatase interface probably creates “hot spots” which work as catalytic sites.

The presence of an ordered array of vertically-aligned TiO₂ nanotubes (produced by anodic oxidation) in the photoanode allowed to improve greatly the performances in the solar PEC cell. In this case the H₂ evolution was of 3.2 mmol h⁻¹ g⁻¹, about one-order of magnitude higher with respect to the activity obtained with the other kinds of thin films. The effects due to the presence of a specific nano-architecture in TiO₂ thin films are multiple: a better light harvesting, lower rate of recombination at the grain boundaries, reduced effects related to formation of a H₂ cap, and faster electron transport and charge separation.

The activity of nanostructured TiO₂ films in H₂ production by photoreforming was a factor of ~6–7 higher than that by water photo-electrolysis, but a similar trend was observed, evidencing that the basic mechanistic factors determining the photoactivity are the same in the two reactions. Fig. 3 evidences this concept by comparing the behaviour in H₂ production by photoreforming and water photo-electrolysis of two nanostructured TiO₂ films prepared by anodic oxidation at different voltages.

As reported earlier by Ampelli et al. (2008) the increase of the anodization voltage during the sample preparation leads to thicker films, but with a larger diameter of the TiO₂ nanotubes and thus less dense packing. The sample prepared at higher anodization voltage resulted in more active H₂ photoproduction. There is a good correspondence between activity increase in water photo-electrolysis due to the different characteristics of the nanostructured film, and photoreforming activity. Fig. 3 also shows a parallel trend for the values of photocurrent generated during the reaction of H₂ production. This confirms the assertion we made above, that it is preferable to indicate the reaction of H₂ production from water on TiO₂ as photo-electrolysis instead of water splitting, as it is often used. The nanostructure of TiO₂ thin film produced by anodic oxidation is strongly influenced from the specific conditions of anodization and, as a consequence, the photocurrent and photoactivity are also considerably dependent on the preparation. The voltage has a relevant role on the nanostructure of titania films. Table 2 reports a comparison of the rates of H₂ production during ethanol–water photoreforming in liquid phase (room temperature) and in gas phase (70°C).

Table 2: Rate of H₂ production for nanostructured TiO₂ thin films with or without Pt and under liquid or gas phase conditions, during photoreforming of 10 vol.% ethanol in water. Temperature: liquid phase 40°C; gas phase 70°C (temperature of the evaporating solution).

Type of experiment	Hydrogen (μmol h ⁻¹)
liquid phase without Pt	12.1
liquid phase with Pt deposited by wet chemistry	47.8
gas phase with Pt deposited by wet chemistry	105.0
gas phase with Pt deposited by photo-reduction	288.0

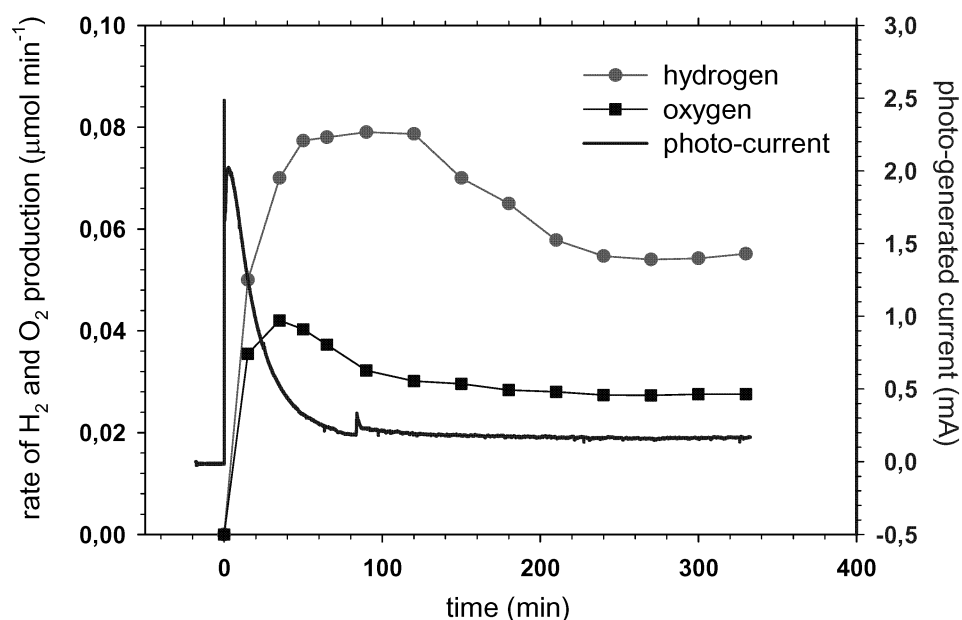


Fig. 4: Rate of H_2 and O_2 production and photo-generated current profiles for a water splitting experiment in the solar PEC reactor with a nanostructured TiO_2 thin film (anodized at 20 V) as photoanode.

It is evident that in gas phase, due to the reduced light scattering by water and more efficient desorption of the adsorbed species which quench the photoinduced mechanism, the rate of H_2 production is one order of magnitude higher than in liquid phase. Gas phase photoreactions in H_2 production are a rather unexplored area, but these results indicate a quite promising area to investigate. Table 2 also evidences the role of the presence and nature of Pt nanoparticles on TiO_2 on increasing the rate of H_2 formation.

The addition of 0.5 wt % Pt to TiO_2 results in a significant increase in the rate of the reaction in both liquid and gas phases, especially when the photo-reduction method is used for manufacturing and depositing Pt nanoparticles. The usual method of deposition by incipient wet impregnations leads to Pt nanoparticles prevalently in the 3–8 nm range, while by photoreduction it is possible to obtain smaller Pt particles (mainly below 2–3 nm) with a minor density and more homogeneous dispersion. This causes an increase of 2–3 times in the rate of H_2 photoproduction, showing the relevant role of this parameter in the preparation of the samples.

Fig. 4 shows the typical profiles obtained from a photo-electrolysis test by using the solar PEC cell. The initial increase of each profile is related to the accumulation of both the gases within each hemi-cell and in the lines to the analytical apparatus. A continuous flow of inert gas (Ar) was sent to the photo-reactor during the experimental tests ($\sim 5 \text{ ml min}^{-1}$), in order to transfer the products to the gas chromatograph instrument for the analysis. Usually, ~ 4 -5 times the residence time is necessary to reach a constant value in transient CSTR-type reactor experiments, e.g. about 2 h in our case. Then, the profiles pass through a maximum and constant productions of H_2 and O_2 are reached after about 2-3 h of time-on-stream. It may be noticed that the maximum in O_2 profile occurs previous to that for H_2 . This could be related to the time necessary to establish the equilibrium through the Nafion[®] membrane, because the two gases are produced separately from the two sides of the PEC reactor. The photocurrent profile instead shows a very sharp maximum after a few minutes, and then decreases, reaching a constant value about one order of magnitude lower than the maximum value. This effect could depend on the fact that, during the initial part of the reaction, the electrons produced in the photoreaction react with oxygen produced from water to form O_2^- species which quench the photoanode activity. According to this explanation, the potential photoactivity of the system in water photoelectrolysis is about one order of magnitude

higher, but limited by the presence of oxygen adsorbed species. Further investigation is needed to better understand the mechanism of the photo-process, so to limit the negative effects (for example, favouring oxygen desorption operating at higher temperatures) and increase the photoactivity.

4.1 The production of solar fuels

In the future energy scenario, the delocalization of the energy production will be an important aspect to deal with; the advantages may be numerous: better integration with territory, reduction of the eco-impact, decrease of fuel transport costs and risks. The production of solar fuels by CO₂ reduction may represent a valid solution towards that direction. We already discussed about the formation of charge separation on suitable semiconductors by solar light absorption to perform the water splitting process; but the electrons and holes generated may further react with water and CO₂ to produce liquid fuels such as hydrocarbons and alcohols (Ampelli et al., 2010; Ampelli et al., 2011a). The reduction of CO₂ can be performed as a two-step approach, e.g. generation of electricity in photovoltaic cells, wind, etc. and then use of the electrons to reduce electrochemically/catalytically CO₂ in a physically separate cell. Alternatively, it is possible a one-step approach by coupling the two processes in a single unit, e.g. a photoelectrochemical/catalytic unit. By using the solar PEC reactor to reduce CO₂, it will be possible in the future to develop “artificial trees” capable of capturing the CO₂ and convert it to liquid fuels. Therefore, the implementation of this concept will allow the reduction of the levels of CO₂ in the atmosphere and at the same time capture a renewable source of energy (solar radiation), transforming it in a form (liquid fuels) which can be stored, used and transformed, thus preserving the large investments made on fossil fuels. The liquid hydrocarbons and alcohols can be alternatively used as chemical feedstocks, or renewable fuels. The solar PEC reactor shows analogies to PEM fuel cells, i.e. can use the R&D on the latter to reduce the costs and improve scale up.

The aspects of the characteristics and properties of the nanostructured TiO₂-based thin films we used as photoanodes have been discussed in the previous section. Here we briefly discuss some aspects of the cathode side, where particularly the conversion of CO₂ (using the protons and electrons generated in water photo-dissociation) is made using special electrocatalysts, based on the concept of nanoconfinement.

The electrochemical utilization of CO₂ has been studied for many years, but many problems exist by using the conventional electrochemical approach (liquid phase), in relation with the solubility of CO₂, type of products formed, stability. These drawbacks have never allowed CO₂ reduction process to pass the lab-stage development (Dubois, 2006). To overcome these problems, we proposed to produce, under solvent-less conditions, liquid fuels such as long-chain hydrocarbons and/or alcohols, which can be easily collected without the need to be distilled from liquid solutions (a quite energy intensive process). We remark that experimentation up to now has been limited to the continuous hemi-cell, working in coupling with an anode compartment filled by a liquid electrolyte, in order to supply the protons (through the Nafion[®] membrane) necessary for the reduction of CO₂ (in gas phase), instead of the photoanode. A constant potential of about -2 V was applied through the cell to supply the electrons necessary for the reaction of CO₂ reduction. The electrolyte is necessary to simulate the half-cell of the full photoelectrocatalytic device, while in the latter no electrolyte will be needed, as the protons and electrons will be produced by water splitting. The features of the electrode used in this gas phase electrocatalytic reduction of CO₂ are close to those used in PEM fuel cells, e.g. carbon black (or carbon nanotubes - CNT) /Pt on a carbon cloth/Nafion[®] assembled electrode (GDE—gas diffusion electrode). On the Pt nanoparticles, the gas phase CO₂ reacts with the electrons and protons to be reduced to longer chain hydrocarbons and alcohols, whose relative distributions depends on the reaction temperature. By using carbon nanotubes, isopropanol is the major product of conversion at 60°C. Good performances are also obtained with Fe nanoparticles instead of a noble metal, although the latter shows a better stability, as shown in the graph of Fig. 5. In addition, it is shown that the use of N-doped carbon nanotubes (N/CNT) allows further improvement in the productivity of making isopropanol. The presence of nanocavities is also important, as it could favor the consecutive conversion of intermediates with formation of C–C bonds.

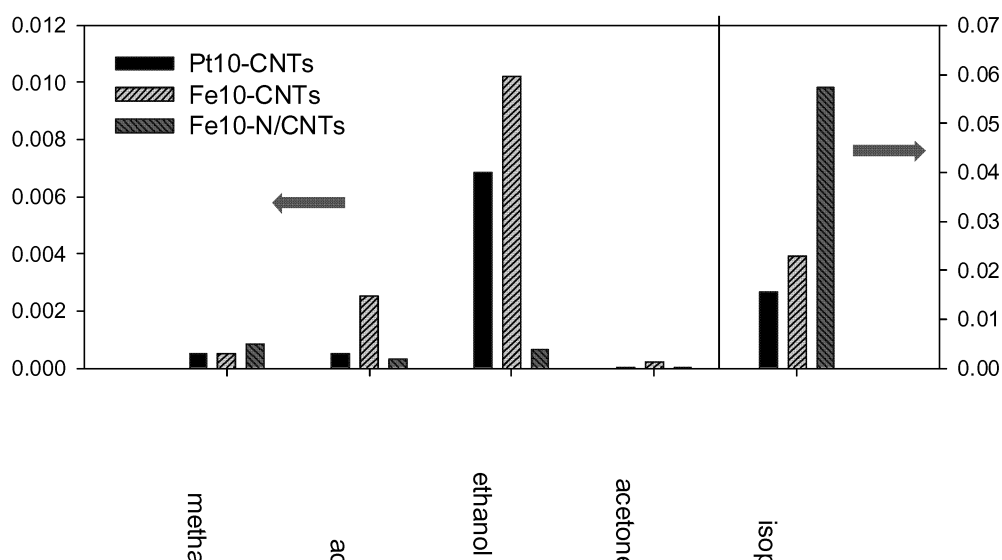


Fig. 5: Product distribution at 60°C in the electrocatalytic reduction of CO₂ in gas phase over Nafion[®]/(Pt or Fe/CNTs)/CC assembly.

5. CONCLUSIONS

In this work we have analyzed some aspects related to the use of a solar PEC cell for sustainable energy production by water photo-electrolysis. For these topics, the main work currently concerns the increase of the efficiency and stability of the photoactive materials used in the PEC system, so to achieve the required efficiency benchmark of 10% that will be viable for its commercial implementation. In order to perform this aim, two parallel lines of research are pursued: the former refers to the synthesis of new materials with characteristics suited to be used as photo-catalysts (band gap extended to the visible region, stability, non-toxicity, low cost etc.); the latter is the correct evaluation of the engineering aspects concerning the photochemical reactor, to achieve an improvement of the process efficiency (irradiation pattern, geometrical configuration, material of construction, heat exchange, and mixing and flow characteristics).

The study of this work integrates two different aspects of the water photo-electrolysis process: the development of novel nano-materials in the form of thin layers to be used as electrodes in a PEC system, and the realization of photo-reactors of new conception which allow to maximize the benefit of the solar light irradiation. The PEC cell takes advantage from fuel cell technology and the core of the system is a membrane electrode assembly (MEA) consisting of: i) a nanostructured TiO₂ thin film (based on ordered arrays of TiO₂ nanotubes) prepared by anodic oxidation of Ti foils, ii) a Nafion membrane[®] and iii) a carbon-based conductive substrate loaded with Pt.

The H₂ photo-production depended on both the geometry of the photo-reactor and the presence of an nano-ordered photocatalyst. The synthesis of a precise nano-architecture is an example of how it is possible to confine the environment of reaction within a very small volume, changing substantially the mechanism of the whole process. This may be considered as the starting point of the design of nano-confined reactors (microreactors) that, alternatively to a conventional batch reactor, allow to obtain several advantages in terms of energy efficiency, reaction rate, yield, selectivity, safety and reliability, facility of scale-up and high grade of process control.

Acknowledgments: Financial support from MIUR under the Italian PRIN-07 Project "Renewable H₂" is gratefully acknowledged.

6. REFERENCES

- Ampelli C., Passalacqua R., Perathoner S., Centi G., Su D.S. and Weinberg G., 2008, Synthesis of TiO₂ Thin Films: Relationship between Preparation Conditions and Nanostructure, *Topics in Catalysis*, 50, 133-144.
- Ampelli C., Passalacqua R., Perathoner S. and Centi G., 2009, Nano-engineered materials for H₂ production by water photo-electrolysis, *Chemical Engineering Transactions*, 17, 1011-1016.
- Ampelli C., Centi G., Passalacqua R. and Perathoner S., 2010, Synthesis of Solar Fuels by Novel Photoelectrocatalytic Approach, *Energy & Environmental Science*, 3, 292-301.
- Ampelli C., Passalacqua R., Genovese C., Perathoner S. and Centi G., 2011a, A novel photo-electrochemical approach for the chemical recycling of carbon dioxide to fuels, *Chemical Engineering Transactions*, 25, 683-688.
- Ampelli C., Passalacqua R., Perathoner S. and Centi G., 2011b, Development of a TiO₂ nanotube array-based photo-reactor for H₂ production by water splitting, *Chemical Engineering Transactions*, 24, 187-192.
- Bockris J.O'M., 2008, Hydrogen no longer a high cost solution to global warming: New ideas, *Int. J. Hydrogen Energy*, 33 (no. 9), 2129-2131.
- Cassano, A., Alfano E. and Orlando M., 2005, Design and analysis of homogeneous and heterogeneous photoreactors, *Chem. Eng.*, 125-169.
- Centi G., Passalacqua R., Perathoner S., Su D.S., Weinberg G. and Schlögl R., 2007, Oxide thin films based on ordered arrays of 1D nanostructure. A possible approach toward bridging material gap in catalysis, *Physical Chemistry Chemical Physics*, 9, 4930-4938.
- Centi G. and van Santen R.A., 2007, *Catalysis for Renewables*, Wiley VCH, Weinheim (Germany).
- Centi G., Perathoner S., Passalacqua R. and Ampelli C., 2011, Solar production of fuels from water and CO₂ in Carbon-neutral Fuels and Energy Carriers, Chapter 4, pp. 291-323, Eds. Muradov N.Z. and Veziroglu T.N., CRC Press (Taylor & Francis group), Boca Raton, FL (US).
- DuBois D.L., 2006, Electrochemical reactions of carbon dioxide, *Encyclopedia Electrochem.* 7a, 202.
- Mills A., Elliott N., Hill G., Fallis D., Durrant, J.R. and Willis R.L., 2003, Preparation and characterisation of novel thick sol-gel titania film photocatalysts, *Photochem. Photobiol. Sci.*, 2, 591-596.
- Mor G.K., Varghese O.K., Paulose M., Shankar K. and Grimes C.A., 2006, A review on highly ordered, vertically oriented TiO₂ nanotube arrays: Fabrication, material properties, and solar energy applications, *Solar Energy Materials & Solar Cells*, 90, 2011-2075.
- Matsuoka M., Kitano M., Takeuchi M., Tsujimaru K., Anpo M. and Thomas J.M., 2007, Photocatalysis for new energy production, *Catal. Today*, 122(1-2), 51-61.
- Yue P.L., 1985, Introduction to the modelling and design of photoreactors, *Photoelectrochemistry, Photocatalysis, and Photoreactors: Fundamentals and Developments*, 527-548, Ed. Schiavello, M., Kluwer.