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Solar Production of Fuels from Water and CO₂: Perspectives and Opportunities for a Sustainable Use of Renewable Energy

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Abstract — *The increasing energy demand, the depletion of fossil fuels and the concern of maintaining clean environment have become the main reasons for a worldwide attention on renewable energy production. Fuel and energy productions from sunlight represent exciting challenges in the next future thank to the recent developments in related technologies, catalysts and materials. It will be discussed the present economic data concerning energy request, the current technological issues required to face an increase of the use of renewable energy, the main drawbacks related to low conversion efficiency in energy applications, the new routes for producing renewable hydrogen and the bio-mimicking approach provided by artificial leaves. Finally, the critical role of nanoscale engineered processes for the development of efficient and cost-effective systems will be evidenced.*

Résumé — **Production solaire de carburants à partir de l'eau et de CO₂ : perspectives et opportunités pour une utilisation durable de l'énergie renouvelable** — La demande croissante d'énergie, l'épuisement des combustibles fossiles et la préoccupation de maintenir un environnement propre sont devenus les principales raisons de l'intérêt mondial pour la production d'énergie renouvelable. Les combustibles et les énergies produites par le soleil représentent des défis passionnants dans un prochain avenir du fait de récents développements dans des technologies connexes, les catalyseurs et les matériaux. Seront examinés les données économiques actuelles concernant la demande d'énergie, les enjeux technologiques nécessaires pour faire face à une augmentation de l'utilisation des énergies renouvelables, les principaux inconvénients liés à la faible efficacité de conversion dans les applications de l'énergie, les nouvelles voies de production hydrogène renouvelable et l'approche bio inspirée fournie par des feuilles artificielles. Enfin le rôle critique de l'échelle nanométrique pour les procédés d'ingénierie de développement de systèmes efficaces et rentables sera considéré.

INTRODUCTION

Energy is an essential component of the strategies to sustainability and security. To address the issues related to the increasing energy demand, the depletion of fossil fuels and the concern of maintaining a clean environment, a marked transformation of the energy system is necessary. Moving from the actual fossil-fuel-centric energy system [1, 2] to a sustainable one based on the efficiency of production and use, and on a large utilization of Renewable Energy (RE) sources [3] requires rethinking the energy system and how to transform the actual system to a carbon neutral, distributed and integrated multi-energy structure.

Solar fuels, where this term indicates fuels produced with the utilization of RE sources and having a carbon negative impact (thus in principle excluding biofuels having an almost carbon-neutral impact) [4-8], play a key role to reach this objective. However, it is necessary to produce liquid-fuel equivalent to those currently in use, in order to allow a progressive introduction in the actual energy infrastructure, without the massive investments necessary to change it, as required for an H₂-economy, for example. The use of carbon dioxide as raw material for solar fuels enables the realization of this objective, and for this reason it is a key element enabling this transformation to a sustainable energy [9] as well as to a resource-efficient, low-carbon society and economy [10-12].

The introduction of RE and raw materials in process and chemical industry is part of this general objective. While this concept has been mainly limited to the use of bio-based raw materials up to now, the combination of CO₂ and RE to produce the raw materials for process and chemical industry will have a great impact on a short-term in transforming the actual production to a new scenario for chemical and energy production based on the synergic integration between CO₂ (re)use, RE and biomass utilization [11, 12]. There are various motivations for this change, from a strategic (the need to have competitive alternative to keep low the cost of fossil fuels, as well as to diversify supplies and suppliers) to environmental and social ones (carbon emission and other environmental and political concerns) and related legislative limitations or incentives.

Although attention in literature on the conversion paths for CO₂ is rapidly increasing [13-18], the attention is mainly focused on the technical and scientific aspects of specific routes of carbon dioxide conversion, without an analysis of their sustainability and impact on the future scenario for energy and chemical production, the integration of these aspects and the opportunities opened for R&D and to meet societal challenges. This perspective contribution aims to discuss these general aspects and how they reflect on new industrial opportunities and on society. The focus is especially on the CO₂ conversion path using RE and the possibilities opened in short-medium term to enable a trading on a worldwide scale of RE equivalent to that actually

present using fossil-fuels (and derived products) as energy vector and raw material source. The products of CO₂ conversion can be the equivalent energy vector and raw material sources for a sustainable future low-carbon society [19-21]. In particular, the presence of a large untapped potential of RE in remote areas will be evidenced. Its use for the conversion of CO₂ (to methanol, for example) can enable an effective transition to a larger share of RE in the energy mix, via long-distance transport of RE. It will be also shown that the potential estimated impact of this technology on the mitigation of climate change is larger than that of CCS (over 7 Gt CO₂ equivalents).

On a long-term perspective, solar fuels and chemicals from CO₂ will be at the basis for a distributed and personalized (economy 3.0) production of energy and chemicals in artificial-leave type devices [22-30]. Here, some advances in this direction will be discussed.

1 SOLAR FUELS AND CHEMICALS FOR THE NEW SUSTAINABLE SCENARIO

The use of solar energy as the backbone for future sustainable energy scenario derives from three basic characterizing elements: clean, cheap and abundant. But solar power is diffuse (ca. 170 Wm⁻²) and intermittent. To go beyond the current limits of its utilization it is necessary to concentrate it for distribution and storage on massive scale. Solar energy can be captured and stored directly in the chemical bonds of a chemical, or “fuel”, and then used when needed (*i.e.* transported and distributed). These solar fuels should be easily transported using existing distribution networks, overcoming current limits regarding long-distance distribution, including for mobile applications, intermittency of RE sources, and utilization in the current energy infrastructure.

Over the last fifteen years the drive to develop systems to produce solar fuels on large scales has been an area of increasingly intense global research activity. Significant progresses in artificial photosynthesis, natural photosynthesis and thermochemical approaches to produce solar fuels have been made [31-37]. In Europe, large interdisciplinary programs have been activated. Some examples are: NANOstructured Photoelectrodes for Energy Conversion (NANOPEC), and Nanodesigned Electrochemical Converter of Solar Energy in Hydrogen Hosting Natural Enzymes or their Mimics (SOLHYDROMICS) projects funded as part of the European Commission’s Seventh Framework Programme (FP7) for research together with SOLARH2, led by Uppsala University in Sweden. This concept of making fuels from sunlight is also now attracting commercial interest, as confirmed by joint initiative involving companies and research institutes like BioSolar Cells, founded by the Dutch government to explicitly develop an incubation structure for

new industrial business, or the Collaborative Research Projects (CRP) sustained by the European Science Foundation's EuroSolarFuels programme.

In the future energy scenario a relevant role is played by CO₂ in term of reduced emissions, re-use, and conversion [38]. Carbon dioxide combined with other materials such water can be transformed into fuels and useful feedstocks using sunlight. The reduction process can either be achieved directly in a photoreactor or indirectly using solar-derived hydrogen as a reductant. The obtained products include carbon monoxide, formic acid, methanol and methane [39-53]. These carbon-based feedstocks together with hydrogen are widely used in industry to make large-volume chemicals, such as fertilizers, pharmaceuticals, plastics and synthetic fuels. Currently, these products (and the energy required to produce them) are based on fossil fuels. The replacement of the traditional (fossil-fuel-based) raw materials and energy sources would have a major breakthrough in reducing carbon footprint of our society. It is out of the scope to discuss here the wide range of possible products and options to convert CO₂, which are analysed in many papers, books and reviews [4, 10-12, 15-18, 33-56]. Here, we may shortly identify three main classes of products:

- advanced materials,
- fine chemicals,
- fuels.

Except for the area of polymers containing CO₂, in particular polyurethanes and polycarbonates, and few other materials in the area of fine chemicals, most of the investigated products are still far from the practical application.

Although there are different motivations, we believe that a general issue derives from the lack of considering the real potential of using carbon dioxide, reactions to target and synergy of the system. The value of CO₂ derives from considering its whole impact on energy and chemical production, and the synergies which can be obtained, including bio-based economy [11, 12]. It is necessary to consider the whole CO₂-economy and address large-scale productions [38], evaluate how CO₂ recycling can become a key element of sustainable carbon-resource management in chemical and energy companies [57], consider CO₂ as the strategic molecule for the progressive introduction of RE resources into the chemical and energy chain [10]. In other words, it is necessary to turn the perspective on CO₂ use, and move from specific cases to a system approach, *e.g.* a CO₂-economy, to really understand the potential of innovation. Some examples will be discussed below.

1.1 Enabling a New Scenario for Large-Scale Trading of RE through Use of CO₂

There are some key concepts which should be shortly introduced to understand this aspect. A first element is the availability on worldscale of very large amounts of unexploitable

RE sources, about 10 TWh only considering hydropower. A main reason is the lack of suitable users around the possible production areas and the actual impossibility to transport on long-distance the electrical energy, the main actual output of RE technologies. The second concept is the intermittency of power output which characterizes several of the current RE technologies, such as solar cells, wind turbines, etc. The third concept is the need of an energy vector (or raw material for chemistry) which is essentially a drop-in product of those used in the actual fossil-fuel based energy (and chemical) infrastructure. The last concept is that CO₂, due to the fact that is low in the thermodynamic energy content scale, is an opportunity to store RE in the process of its transformation to more valuable (higher energy content) chemicals or fuels. Therefore, there is a unique opportunity to combine all these aspects in the challenge of enabling a new scenario for large-scale trading of RE through CO₂ use.

There are different routes to convert and utilize CO₂, the most relevant of which (to achieve the above objectives) involves the hydrogenation of CO₂ to form oxygenates and/or hydrocarbons. Possible energy vectors that derive from the hydrogenation of CO₂, either directly or through the intermediate stage of the Reverse Water Gas Shift (RWGS) reaction, are the following:

- formic acid, which may be used in formic acid fuel cells or as a vector to store and transport H₂ (the reaction of synthesis is reversible, and formic acid can be catalytically decomposed under mild conditions to form back H₂ and CO₂);
- methanol and DiMethylEther (DME);
- methane (Substituted Natural Gas, SNG);
- >C1 alcohols or hydrocarbons.

The main routes are chemical (catalytic), but electrochemical or solar thermal routes are also possible, even if the latter two routes are still not sufficiently developed. Syngas may also be produced by reaction with hydrocarbons (particularly methane) through the so-called dry reforming. However, dry reforming is an endothermic reaction occurring at high temperature (about 900-1000°C) and with formation of carbon (which deactivates the catalyst) as a side reaction.

The catalytic chemistry of the RWGS reaction, the following transformation to methanol/DME, or hydrocarbons via Fischer-Tropsch synthesis, and the subsequent production of gasoline (Methanol To Gasoline, MTG) or of Diesel via hydrocracking of the alkanes produced in the FT process (using Co-based catalysts) is well established, even if there is still need for development because of the change of feed composition starting from CO₂ rather than from syngas. Also, in terms of process development, most of the necessary knowledge is available.

Between these different routes, we consider preferable the production of methanol from CO₂, due to the efficiency and high selectivity, the formation of a liquid product highly

versatile in utilization, safe and easy to transport and distribute, well integrable within the actual infrastructure. However, there are also different opinions.

There are various possible routes to produce methanol from CO₂ using RE sources. We will call here Renewable Methanol (RM) that deriving 100% from fossil-fuel-free sources. Both the H₂ utilized in the process is produced from water and RE, and the CO₂ derives from non fossil-fuel sources, for example by biomass fermentation. RM is a negative carbon footprint product, reducing of over 70% the carbon footprint (on Life-Cycle-Assessment, LCA, bases) with respect to the “conventional” methanol produced today mainly from natural gas. Also with respect to biofuels, the carbon footprint is about 30% lower (on equal energy content), allowing to move from almost carbon-neutral biofuels to really carbon-negative fuels. RM can be produced ideally from the photocatalytic or PhotoElectroCatalytic (PEC) reduction of CO₂, with the electrons and protons needed for this reaction generated by water photoelectrolysis. However, the actual production rates are still too far from those necessary for possible exploitation, even in medium term. Similarly, the electrocatalytic reduction of CO₂ to methanol is still quite far from the possible application on large scale [58, 59]. The only current route involves the catalytic conversion of CO₂ by heterogeneous catalysis [57, 60]. Several attempts, some also rather interesting, have been made to realize this process in liquid phase using homogeneous catalysts [61]. However, when the rates are analysed in terms of the industrially relevant parameters (*e.g.* productivity per reactor volume, instead that turnover frequency or number) and production costs, there is a factor of over two order of magnitude to overcome. In the short-term, also this route appears not feasible. On the other hand, methanol is currently produced in about 60 Mtons per year by heterogeneous catalysis, at reaction temperatures about 220°C and pressures of about 70-100 bar, but starting from syngas (CO/H₂ plus some CO₂ up to a maximum of about 3%). Cu/ZnO/Al₂O₃ are the base elements of the catalysts. These catalysts are also active in RWGS, thus in principle able to operate from CO₂/H₂ mixtures, but productivities are significantly lower. There are two main problems to overcome. First, the CO₂/H₂ mixture is more oxidizing than the CO/CO₂(3%)/H₂ altering the active state of the catalyst. Second, the higher formation of water inhibits reversibly the reaction. However, by suitable doping it is possible to overcome these problems, even if a further improvement in productivity to methanol could be necessary.

The more severe actual limit regards the pressure, although often not accounted in several literature studies. To have enough productivity and conversion in methanol synthesis from CO₂, it is necessary to operate at pressures at least above 50 bar, but compression of H₂ may raise costs above an acceptable level. It is necessary to produce H₂ already at this pressure. Actual photochemical routes (water

splitting, etc.) are all operating at near ambient pressure, as well as thermochemical and biological routes [62-65]. In addition to the still very low productivity (about 100 times lower than necessary), the pressure gap is a relevant issue. The only technology available in the short-middle term (except perhaps the production of H₂ from biowaste) is the water electrolysis, either at low temperature (around 70°C) on PEM-type electrolyzers or at higher temperatures (above 600°C) on Solid Oxide Electrolysis Cells (SOEC) [66, 67]. However, current technologies do not allow stable operations above about 30 bar. It is thus still necessary to improve technology and electrocatalysts in these devices, as well as to reduce overpotential, for example by a better design of the electrocatalysts [68].

Hydropower is the preferable source of RE to consider in first instance to estimate the feasibility of a new scenario for large-scale trading of RE through CO₂ use. There are various motivations. Hydropower is the largest renewable source, accounting for about 80% of the actual world renewable electricity generation. The global technically exploitable hydropower potential is estimated to be over 16 PWh per year, but nearly 80% of which not currently exploitable being in remote areas missing of the necessary local uses and too far to be transported to other areas by grid. A wide part of this hydropower potential can be utilized only if effective ways to transport this unused RE over long distances will be developed.

In addition, hydropower is the cheapest production of RE on a large scale, is a ready technology, and it provides a nearly constant energy supply, differently from most of the alternative RE sources (wind, solar, etc.) that are intermittent. The latter aspect has a relevant feature for cost estimation. In fact, the fixed costs of the technology (which account for up to 70% of the overall cost) for converting electrical energy to chemical energy (methanol), can be amortized over the entire year for a constant RE source, such as hydropower, but only for a fraction of year for the discontinuous ones (*i.e.* wind and solar).

A techno-economic assessment of the cost of production of RM by this route (CO₂ transport in remote areas, where H₂ can be produced at low cost from hydropower, conversion of CO₂ to methanol and finally transport back of RM) was made by Barbato *et al.* [69]. Figure 1a schematically illustrates the concept of remote production of methanol from CO₂, where cheap sources of electrical energy (by hydropower) exist, which can be utilized to produce H₂ and then RM. Carbon dioxide is transported there (by ship, for example) and RM transported back. The difference of energy between RM and CO₂ is nearly the imported RE. In fact, the energy loss due to transport is quite limited and there is a minimal loss of energy in the conversion of CO₂ to methanol. The main loss is associated to the production of H₂ itself by electrolysis.

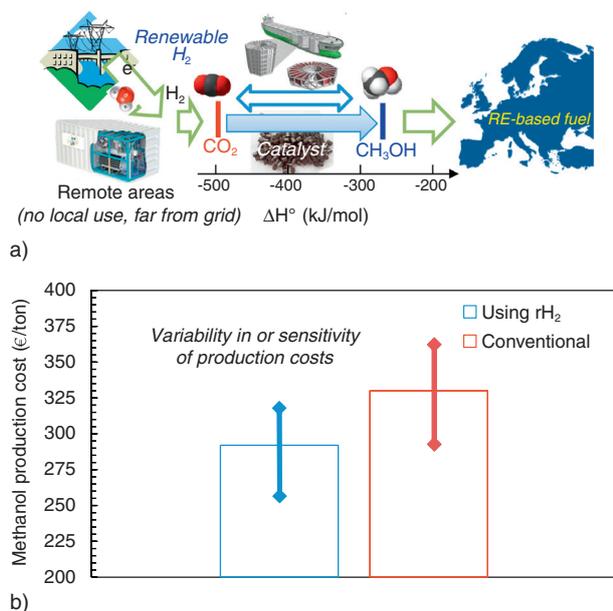


Figure 1

a) Simplified illustration of the concept of remote production of methanol from CO₂. b) Estimated cost to produce RM by this route, based on a cost of production of H₂ of 0.140 € Nm³ H₂, in comparison with market contract price for methanol produced by "conventional" route (from natural gas). See text for comments regarding variability in or sensitivity of the production costs. Based on the data in Reference [69].

Figure 1b reports the estimated cost to produce RM by this route, based on a production cost of H₂ of 0.140 € Nm³ H₂ [69]. The arrow in the bar represents the sensitivity variation of production cost with respect to a cost of carbon dioxide at site of 20-70 €/ton and of an electricity consumption for H₂ production between 3.8 and 4.8 kWh/Nm³ H₂. The arrow in the bar for "conventional" RM cost represents the variability in market contract price (in Europe, Aug. 2013). Although these are estimations, and market price is highly variable and depends on many factors, the message in Figure 1 is that it is already possible today to produce RM and trade/import RE on world scale by using this technology, when low-cost electrical energy is available.

The potential RE from hydropower that can be potentially exploited by this technology is about 10 PWh per year of electrical energy, which correspond to a reduction of about 7 Gt of CO₂ equivalent emissions [69]. Figure 2 reports an estimation of the potential contribution to the reduction of CO₂ emissions for Europe by year 2050 for:

- Carbon Capture and Sequestration (CCS),
- the use of biofuels (average contribution, not considering land change use and other aspects such as intensified

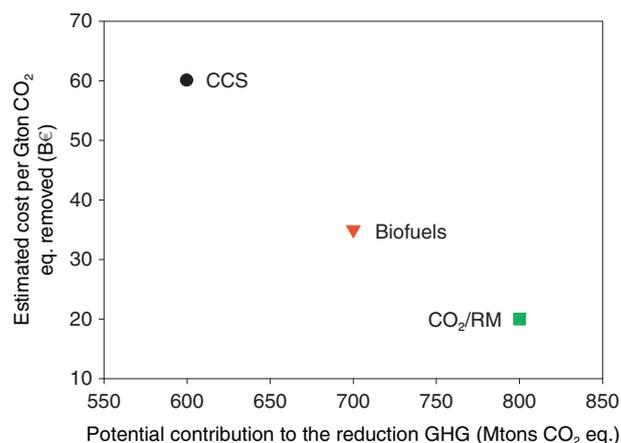


Figure 2

Estimation for Europe by year 2050 of the potential contribution on the reduction of CO₂ emissions by CCS, use of biofuels and CO₂/RE. Based from the data in Reference [69].

GreenHouse Gases (GHG) emissions due to the enhanced use of fertilizers consequent to monocultures),

- importing RE by conversion of CO₂ to methanol (trade RE).

It also shows the comparison of the estimated cost per Gt CO₂ removed for the three cases of CCS, use of biofuels and Trade RE via CO₂/CH₃OH [69]. This result evidences that the impact on the mitigation of climate change by this route is large, up to potentially 8 Gt CO₂ equivalents, and at least comparable with that of Carbon Capture and Storage (CCS) and biofuels.

Therefore, the proposed (CO₂/RE) technology is a cost- and environmentally effective solution for the reduction of GHG emissions ensuring:

- reduced emissions of pollutants (NO_x, SO_x, etc.) and GHG emissions, in fact, the use of unexploited RE sources decreases the needs of new power plants as well as of fossil fuel extractions;
- better diversification of energy sources (with benefits in terms of energy security) and greater flexibility in use (for example in the transportation sector);
- better flexibility in energy management to follow fluctuating energy demand, (for example, resorting to methanol-fuelled turbines).

Methanol-fuelled turbines have a rapid switch off-on time; and methanol is considered a superior turbine fuel (even if the system must be modified), with low emissions, excellent heat rate, and high power output.

The conversion of CO₂ to methanol (CO₂/RE) results in the production of energy vectors and raw materials for chemical production, making it possible to trade RE, to reduce

fossil fuel consumption and contribute to Climate Change Control (CCC). RM may be considered a promising technology for commercialisation, even though a more in depth analysis of economics and some technology development are necessary.

1.2 Moving on the Technology Path for Solar Fuels

As remarked before, a systemic rather than reaction-specific approach is required to understand the real impact of CO₂ utilization, which should be analyzed not only in terms of the “traditional” techno-economic assessment. For this reason, it is relevant to discuss shortly also the technological path for the developments in this area, although a more detailed discussion is out of the scope. A first aspect regards the further developments needed to improve the preparation of solar fuels from CO₂.

We may shortly identify three main steps, although each has various sub-topics and challenges to be developed. The first one, which is currently available, is based on a 3-step approach. Electrical energy (ee) is produced using RE sources (step 1), and it is then used to produce H₂ in electrolyzers (step 2). Finally, H₂ is employed in catalytic processes, either homogeneous or heterogeneous, to convert CO₂ to different possible products, such as C1 (formic acid, methane, methanol) or >C1 chemicals (alcohols, DiMethyl-Ether, light olefins, hydrocarbons, etc.). The products could be used either as energy vectors or as base chemicals for industry. If cheap electrical energy sources are available (cost lower than about 0.05 \$ per kWh), converting CO₂ by this approach may be already competitive, as demonstrated in the previous section. The clean RM process developed by the Carbon Recycling International (CRI) in Iceland is an example of industrial application, although very strongly dependent on local situation (geothermal energy). Other companies such as *Mitsui Chemicals Inc.* with their “Green House Gases-to-Chemical Resources” technology are active in this field, but with focus on hydrocarbons (via Fisher-Tropsch - FT - reaction) rather than methanol. A modification of FT is the conversion of CO₂ to olefins (Fischer-Tropsch to Olefin, FTO), which also may be interesting, when low-cost H₂ from renewable sources is available [12].

The main elements of this first approach are available, but there is still the need to develop improved catalysts (for CO₂ conversion to methanol or methane, for the reversible synthesis of formic acid to store H₂, etc.) as well related technologies (for example, compact devices using microreactors for power-to-gas or to methanol conversion). It is also necessary to improve the efficiency of electrolyzers, their scalability and stability, particularly under high-pressure operations. Advances in cell engineering and electrocatalysts design are also required, starting from the understanding on how

to decrease the overpotential in H₂ generation from water electrolysis. Reasonably it can be assumed that about 5 years could be necessary to get these targets. Cost reduction of electrolyzer technology and avoid the use of noble metals in electrodes are further targets to be achieved.

The second class of routes includes electrochemical or electrocatalytic 2-step processes characterized by an intermediate production of electricity. This approach may be considered to be realized in medium-long term, e.g. between 5 and 10 years. A possibility is to develop inverse fuel cells, where CO₂ is directly fed on a special designed cathodic electrode, able to convert directly CO₂ using protons supplied by water oxidation from the anode and electrons coming externally from a RE source. The other one involves an electrocatalytic process, in which the adsorption and transformation of the reactant on the electro-catalyst occur according to a more complex mechanism [70-72]. This approach requires to integrate the catalysts for water oxidation (to O₂, protons and electrons) with the catalyst for H₂ generation (using the protons and electrons generated in the other step) in a PhotoVoltaic (PV) cell. There are already advanced studies in this direction (solar/H₂/chemical) but it is necessary to have a breakthrough in the productivities and cost/efficiency. Devices, in which physically separated productions of O₂ and H₂ occur, are necessary for safety and cost motivations. This aspect requires a diverse design with respect to that of devices currently investigated, and the availability of a proton-conductive membrane to separate the reactions producing O₂ and H₂.

There is the need to develop more productive and stable catalysts for water oxidation, while the catalysts for H₂ evolution are less problematic. The hydrogen produced in these devices is then used for the catalytic conversion of CO₂. It may be estimated that, within a decade, the production of H₂ from renewable sources (including from biomass, [73]) by this route at competitive costs (less than 2-3 \$ per kg) should become available.

In a longer-term perspective, it is necessary to carry out a fully integrated artificial leaf-type solar cell, where a photo-anode able to photo-electrolyze water using sunlight (PEC – solar cell) is present. This is the third class of routes in which the transformation of RE to fuels or chemicals is made directly in a single (integrated) device. Photochemical processes realize on a nanoscale the separation between the processes of generation of protons/electrons from water using light and those of reduction of CO₂ using protons/electrons. The same concept was obtained on the mesoscale in PEC solar cells with the physical separation of the two processes in different compartments allowing the decrease of self-quenching effects and the separation of the products formed at the anode (O₂) from those formed at the cathode (products of CO₂ reduction), with consequent safer operation conditions. Some further aspects will be discussed in the following section.

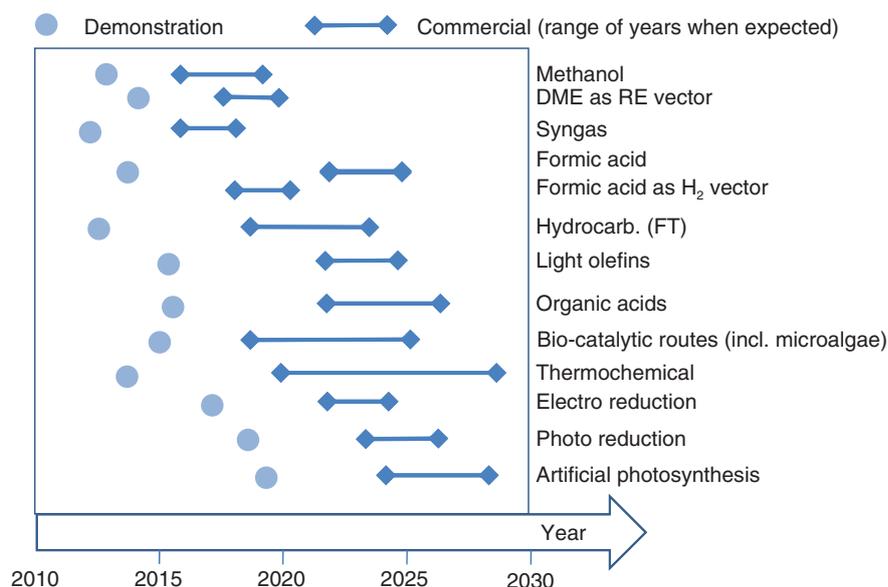


Figure 3

Estimated “technology roadmap” for commercialization of CO₂ re-use paths. Adapted from Figure 5 in Reference [9].

With respect to natural leaves, these artificial devices should allow an intensified production, be cost-competitive and be able to tune the conversion of CO₂ to the specific required products (fuels, chemicals). Their use will allow a distributed energy (or chemical) production, but there are many challenges in terms of electrocatalysts, nanodesign of elements and interfaces, charge transport and separation, etc. It is thus still a vision, whose realization should be possible only through the development of the next-generation catalysts, nanomaterials and nanosystems for energy. The realization of this vision and related knowledge on materials, nanodevices and catalysts can thus become one of the driving factors for a sustainable future of the chemical industry, because this area has the potential to become a game changer for chemistry.

There are many additional routes under development related to the broad area of solar fuels, with the limits of definition of this term indicated in the introduction. Figure 3 reports the estimated “technology roadmap” to commercialize CO₂ paths to solar fuels and chemicals. This roadmap is based on the evaluation of those presented by different institutes [74-81] corrected taking into account the results of recent workshops, meetings, reports etc. as well as considerations regarding the possible market, costs for implementation of the technology, perspectives in incentives on re-use of CO₂ in relation to the different impact of the various technologies, drop-in characteristics of the technology/products, exploitability and technical constrains, etc. In Figure 3, the light blue circle represents the technology at

pilot/demonstration scale, while the bar represents the expected time frame when commercial operation of the technology is likely. Due to different uncertainties in the conversion paths, the range of years when commercial operations will start changes from path to path.

Table 1 reports some specific examples of technologies beyond the fundamental research stage in the area of CO₂ to solar fuels and chemicals, although it should be mentioned that as for all these new areas, dominated from venture capital companies rather than large one (although all the large energy companies have active projects in the area), advertisements are higher than real demonstrations. It is thus often difficult to understand the real potential.

2 TOWARD ARTIFICIAL LEAVES

As introduced in the previous section, the design and construction of artificial-leaf type devices able to ideally utilize CO₂ (eventually captured directly from air), water and sunlight to produce tailored fuels and chemicals are the end of the transition to a new sustainable energy/chemical system. For this reason, it is a long-term (>15 years) objective, whose realization requires to start already in building the fundamental knowledge necessary to realize efficient, stable and cost-effective devices. Many activities are on-going on these aspects, as commented before and further in the reviews [82-113].

TABLE 1
Examples of technologies beyond the fundamental research stage

| Organisation | Fuel product | Technology status |
|---|---|---|
| <i>Carbon Sciences</i> , US | Light hydrocarbons (via FT process) | Moving from laboratory towards commercialisation |
| <i>Joule Unlimited Inc.</i> (Joule), US | Ethanol and Diesel equivalent products (via microalgae) | Moving from laboratory towards commercialisation |
| <i>Mantra Venture Group</i> (Mantra), Canada | Formic acid (electrocatalytic) | In negotiations for first commercial demonstration |
| <i>Carbon Recycling International</i> (CRI), Island | Methanol (using geothermal energy) | First commercial plant completed at the end of 2012 |

Although important aspects related to the mechanism of light harvesting, charge separation and transfer, mechanism of water oxidation and nature of the active elements, etc. are discussed in the cited reviews and related works, we should observe that most of the studies on artificial photosynthesis are limited to the steps of H₂O conversion to H₂ and O₂ rather than to consider the conversion of CO₂. Although these studies contribute significantly to the advance of the knowledge, many of the proposed devices cannot operate in the presence of CO₂ but rather in water splitting. In addition, a large part of the studies on artificial photosynthesis or artificial leaves deals on the single molecular elements to realize a specific step of the whole process, with few of them investigating also the supramolecular assembling of the different functionalities, while a system approach is necessary to correctly address the topic.

Molecular assemblies bio-inspired from photosynthesis have been studied by various research groups [86]. These systems typically contain a chromophore, such as a porphyrin, which perform the first step of light harvesting. These molecules are covalently linked to one or more electron acceptors, such as fullerenes or quinones, and secondary electron donors. After chromophore excitation, the photo-induced electron transfer generates a primary charge-separation state. Electron transfer chains spatially separate the redox equivalents and reduce electronic coupling, slowing recombination of the charge-separated state to make possible their use in the redox catalytic processes. The reaction rates of the latter are typically two orders of magnitude slower, or more, than charge creation/separation processes. This aspect is the critical issue in artificial photosynthesis processes, because these charged species, if not fast consumed in the redox processes, can recombine (reducing the overall efficiency) or give rise to side reaction, including degradation of the (supra)molecular system for light-harvesting, charge separation and redox catalysis. This is one of the reasons why inorganic systems, which are more robust, are typically necessary, while organic complexes and supramolecular systems, which are better to develop

and optimize as well to understand, have failed (in over twenty years of studies) to produce practically applicable artificial photosynthesis systems. Nevertheless, it has to remark the significant progresses made in many aspects, particularly on the development of:

- antenna systems, employing a variety of chromophores that absorb light throughout the whole visible spectrum, in order to increase overall efficiency,
- advanced catalytic redox centers with high turnover number.

More limited progresses have been instead made on the incorporation in the supramolecular assemblies of control and photo-protective elements borrowed from photosynthesis, although this is a key factor for the long-term stability.

The concept of artificial leaves, differently from artificial photosynthesis, is focused on the system architecture as basis for the design of the devices, rather than on the development of the single elements and their subsequent assembling into a functional device. The different perspective implies a higher consideration on the system functionality, rather than on that of the single elements, but in PEC devices, *e.g.* artificial leaf, there is a mutual influence. The behavior of the system is not the sum of the single components. In addition, a system approach emphasizes aspects such as charge transport and system reliability, which are instead less investigated in artificial photosynthesis approach. These aspects are amplified in importance in moving from water splitting to the more challenging PEC conversion of CO₂.

Another comment regards the necessity or not to have a bio-mimicking or bio-inspired approach, which has been typically highlighted in most of the cited reviews. Nature taken over billions of years to develop and optimize the highly complex machinery present in leaves that enables the use of sunlight to oxidize water and produce electrons/protons used in a different part of the cell to reduce CO₂. To remember that the products of carbon dioxide reduction are the elements (carbohydrate, lipid, other organic species) necessary for plant life and growing, while in Artificial

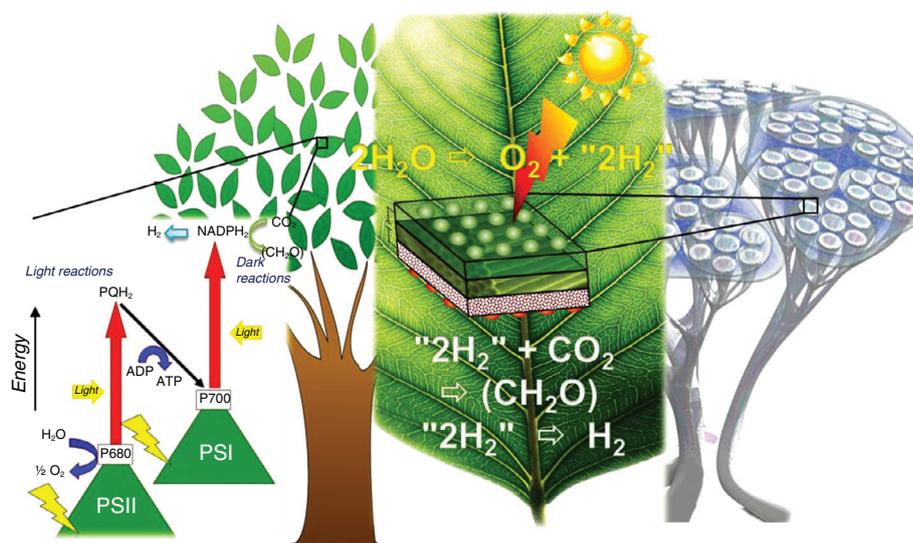


Figure 4

Going from natural to artificial leaves requires using a radically different system design taking inspiration from nature, but developing conceptually new and robust devices which overcome the limit of natural leaves. “2H₂” indicates the four protons and electrons produced in the water oxidation step (they are equivalent to two hydrogen molecules), while (CH₂O) indicates in general the products of CO₂ hydrogenation, which include C1 and >C1 hydrocarbons, alcohols and other organic species.

Photosynthetic Leaves (APL) the aim is to produce fuels or chemicals. In addition, plants are characterized from a series of mechanisms which allow to limit the rate of the processes (for example, light absorption) which otherwise could damage the plant itself. In artificial devices, it is necessary instead to intensify the processes, at least of one or more order of magnitude, to improve the cost-effectiveness. Therefore, the development of efficient, cost-effective artificial systems requires a new functional and robust design to realize two goals:

- intensify the process, thus allowing a higher productivity and efficiency in converting sunlight;
- use solid components which keep functionalities, but are more robust, scalable and cost-effective.

This concept is exemplified in Figure 4.

2.1 Development of PEC/Artificial Leaf-Type Solar Cells

There are various constraints, which have been typically not accounted or only in part, in cell design and characteristics derived from analysis of cell usability. These aspects have to be included already at the initial stage of cell design, because they determine the choice of the materials and their needs. An important aspect is that the products of oxidation (O₂) and reduction (H₂, or the products of CO₂ reduction) have to be produced in separate zones of the cell, to avoid

safety problems, costs of separation, quenching effects. It is also necessary to have continuous operations, with easy recovery of the reaction products. In terms of usability of the cell, avoiding liquid electrolytes may be necessary to facilitate the recovery of the products, but also for stability of electrodes/cell elements and sealing. A very important element, typically not considered, is that the cell should operate with stable performances above 50-60°C, or preferably higher temperatures. It should be considered the temperature increase during exposition to sunlight, especially when a light concentrator is used to improve cost-effectiveness of the cell. The utilization of cooling systems is not possible. A final obvious aspect is that it is necessary to have a compact design, easily scalable.

These constraints determine the cell design/engineering and in turn the characteristics required for the cell elements, such as electrodes and catalytic components. However, most of the literature studies do not account for these aspects, for example, stability/performances at higher temperature than room temperature, separation of the reaction products and productivity per unit cell dimension. There are three main aspects, in particular, to take into account in the design of cells for solar fuels:

1. It is necessary to produce liquid fuels, which can be easily removed and separated; producing H₂ is not the suitable approach, but rather it is necessary to produce

- protons/electrons used to selectively convert CO₂ to alcohols or hydrocarbons (or eventually to produce syngas);
2. It is mandatory to produce O₂ (from water splitting/photoelectrolysis) in a separate compartment with respect to that where the reduction occurs (formation of H₂, products of CO₂ conversion). There are many motivations, including safety, separation costs, product intensification, quenching effects, etc. PEC approach is thus mandatory.
 3. The cell should have stable operations above room temperature, about 70–100°C or even higher temperatures (about 150°C or higher), when the cell operates coupled to a solar concentrator.

Practical implementation of PEC solar cells requires focusing attention on different aspects than those usually investigated, such as the following:

- productivity intensification (to improve cost-effectiveness);
- robustness even with temperatures higher than room temperature and eventually under pressure (necessary to achieve the first goal);
- chemical inertness (nascent O₂ or H₂O₂ on one side and electrons on the other side of PEC device are very reactive species);
- low cost of construction and use of non-rare materials;
- selectivity in the nature and distribution of the products obtained by CO₂ reduction, and in avoiding side reactions such as H⁺/e⁻ recombination to give H₂ (rather than hydrogenate CO₂).

To overcome the main drawbacks related to low sunlight-to-fuel photoconversion efficiency and selectivity, a deeper understanding of mechanisms of reaction is required, in order to develop highly active photocatalysts, for what concerns adsorption of reactants, light harvesting, charge separation and transport, and CO₂ activation.

However, recent investigations, conducted by DRIFT spectroscopy and ¹³C labelled CO₂ on photocatalytic CO₂ reduction over copper oxide promoted titania, have evidenced the participation of catalyst associated carbon residues and surface adsorbed water in the formation of CO₂ reduction products, suggesting to perform activity tests in future studies, to exclude the participation of carbon residues in the formation of CO by CO₂ photoreduction [114]. Even if clear evidences that CO is formed in the absence of carbon residues have been provided in isolated sites in Ti silicalite sieve by Ulagappan and Frei [115], in CO₂ reduction reactions performed under ¹³CO₂ and H₂O which showed solely ¹³CO production, additional insights on reactive adsorption limits of CO₂, effect of surface hydration, presence and nature of species which can prevent efficient light activation of the catalyst and on the extent of water induced photocatalytic surface carbon gasification should be considered, in order to avoid overestimation of the rate of the artificial

photosynthesis reactions over these materials, as well to further reveal the chemical pathways of CO₂ reduction.

The solar-driven goal in reduction of CO₂ to value-added chemical fuels is to synthesize photoactive materials able to perform the redox reactions and achieve conversion efficiency and selectivity that exceeds Nature's photosynthesis [116].

In pursuing this aim, long-time challenges have been opened in the field of catalysis intended to gain a deep understanding of surface/interface-reaction processes in order to develop novel and efficient (photo)catalysts sensitive to sunlight.

It is difficult in some cases to compare results obtained in different media and reaction conditions. Beneficial effect on CO₂ investigation derives from several studies conducted so far in heterogeneous systems. The most explored semiconductor materials for photocatalytic reduction of CO₂ include metal oxides (TiO₂, titanates, tantalate, niobate, tungstate, etc.), metal sulphides (CdS, ZnS, MnS and Cu₂ZnSnS₄), nitrides (Zn_{1+x}Ge)(N₂O_x), and phosphides (*p*-InP, *p*-GaP) [31].

Recently, significant contributions in (photo)catalyst development have come from the multidisciplinary areas of material science, surface chemistry, nanotechnology, semiconductor physics and engineering, with research activities concerning:

- the electronic band-structure engineering by several techniques: quantum confinements, cation or anion doping, solid solution formation, sensitization, etc. All of them are devoted to adjust bandgap and band edge position for a wider light-harvesting and a more efficient utilization of solar energy. Also optical approaches have been applied, direct to favour light scattering to increase the optical path length, or to obtain an usable visible photon by doping with up-conversion materials able to convert two (or more) non-absorbed NIR photons;
- the possibility to arrange the materials in form of crystalline nanostructures to decrease the electron-hole recombination rate and provide direct pathway for electron transport, combined with the use of co-catalysts to lower the barrier for CO₂ activation, and to affect product selectivity and Z-scheme of heterostructures to realize the spatial separation of photoexcited e⁻/h⁺ pairs contributing to inhibit their recombination, and ultrathin geometries [117, 118] which promote charge carriers fast migration from the interior to the surface to participate in the photoreduction reactions;
- crystal orientation, which could influence surface energy and active sites, and modify the electronic band structure of the catalyst favouring the preferential adsorption of reactants and intermediates;
- surface oxygen vacancy engineering, which favours CO₂ adsorption and activation [116] and influences the surface

chemistry of semiconductors by changing and tuning their electronic and chemical properties; hierarchical structures, on multimodal macro-/meso-/microporous scale, characterized by easily accessed channels, shape selectivity and large surface areas which contribute to enhance reactants adsorption and to supply more surface active sites significantly enhancing gas-phase reaction efficiency. However, gas diffusion limitation is still a problem and also electrical conductivity and diffusion length of photocatalysts should be further enhanced. In some cases use of gas diffusion electrodes has been found to improve mass transport with beneficial effect on product formation rate of and selectivity [117, 119, 120].

Using electrocatalysts to reduce CO₂ dissolved in liquid, CO₂ concentration in the electrolyte and mass transport are decisive factors in determining the Faradic formation efficiencies of the different products [121].

Low temperatures are generally chosen, because performing the reaction at lower temperatures enhances CO₂ solubility as well as stability of the reduction intermediates. Whereas at higher temperatures, the selectivity to C1 products reduces and that to C2 products increases [122].

In electrochemical systems, in the attempt to overcome the problem related to the low solubility of CO₂ in aqueous solutions (33 mM at 25°C at 1 atm CO₂), organic aprotic solvents are often used as electrolytes [31]. In these nonaqueous electrolytes, the solubility of CO₂ is high but poor solution conductivity determines high ohmic losses [121]. Using nonaqueous electrolytes it is also possible to work below freezing point of water, and hence the benefit of increased solubility at low temperatures can be exploited [123]. Moreover, in nonaqueous solutions, hydrogen evolution is severely suppressed, especially at lower temperatures, and hence current faradic efficiency for CO₂ reduction is generally higher. Further, while Hydrogen Evolution Reaction (HER) and CO₂ reduction proceed in parallel competitively in aqueous electrolytes saturated with CO₂, hydrogen evolution is suppressed in nonaqueous solutions, especially at lower temperatures, and hence the current efficiency for CO₂ reduction increases.

Further useful insights may come from integrated experimental and computational research approaches to evaluate catalyst activity toward CO₂ photoreduction.

It is also beneficial pay more attention to the deactivation phenomena in the photocatalytic reduction of CO₂, attributable to:

- the adsorption or accumulation of intermediate products on the semiconductor surface which decreases the available reaction sites and also hinders the adsorption of CO₂ or H₂O, leading to semiconductor deactivation especially under the continuous irradiation;

- the desorption of the produced hydrocarbons which can affect adsorption of reactants and take part in the photocatalytic reaction;
- the surface contamination of semiconductors which can reduce light absorption.

All these aspects, up to now, have been only partially investigated and the described phenomena, at various extent, can affect the efficiency and rates of CO₂ photoreduction.

While encouraging progresses have been achieved toward CO₂ conversion, in all the described studies photo (and electro) -driven catalysts functionalities have been developed separately, independently from the cell design and/or not considering cell requirements. Although bio-mimicking approach provides inspiration, a radically different strategy, particularly in terms of system design, is required. Smart, cheap and robust devices are necessary. The use of inorganic materials would be essential, because most of the investigated molecular complexes are too costly, not robust enough and/or require special reaction conditions. Critical elements to consider, already at the initial stage, are selection and composition of artificial leaf elements (catalysts, electrodes, membranes, sensitizers) and cell engineering for which a system design approach is essential.

Therefore, the limits of natural systems should be overcome by designing conceptually different devices, but studies in this direction are still limited, notwithstanding the large number of publications around the concept of artificial photosynthesis and photosynthetic devices. Some of the critical aspects to consider are the following:

- nanoarchitecture of electrodes [124], in particular how to develop specific functional nano-architectures by mastering nano-objects and controlling charge flow [125];
- system design in approaching PEC devices to maximize cost-efficiency, productivity and charge transport;
- the role of catalysis in the design of these advanced PEC devices.

Many novel synthesis procedures for nanomaterials, including for energy applications, are available today, as reported, although effort is still necessary for a better understanding of the relationships between nanoarchitecture and functional behavior. In addition, the characteristics of these nanomaterials are often not linked to the specific needs for the design of advanced PEC solar cells. The simplified scheme of a PEC solar cell with above characteristics is shown in Figure 5.

Various attempts were made recently on the development of advanced design for artificial leaf solar cell, such as the one of the Helios Solar Energy Research Center (Helios SERC). The general idea is to develop membrane-based assemblies of oriented PEC cells with geometry similar to that of the natural photosynthetic system. The tubes are the embedded nano PV centers. A catalyst that oxidizes water

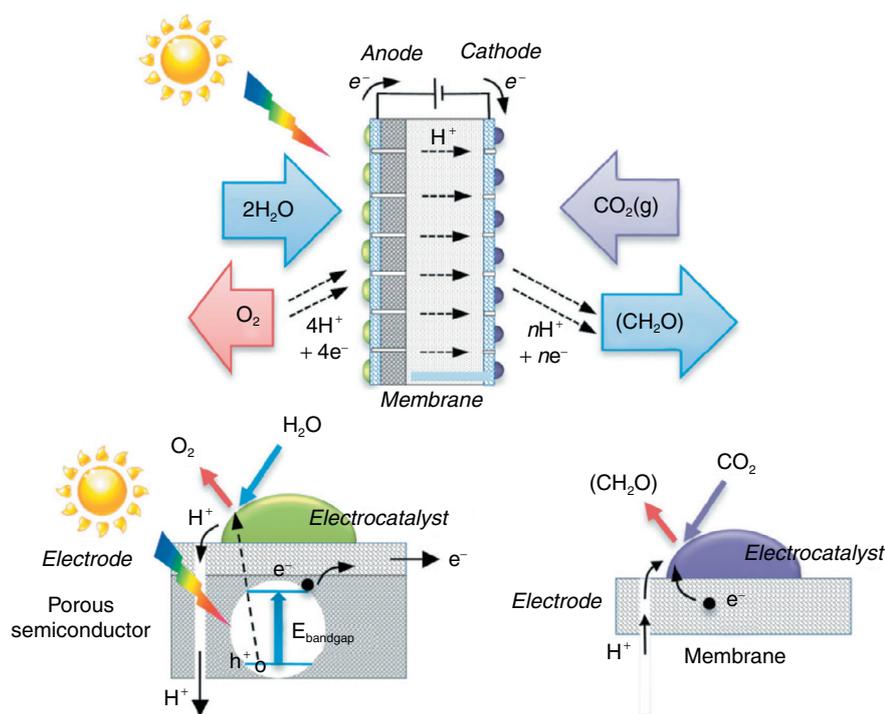


Figure 5

Simplified scheme of a PEC cell with compact design and suitable for operations at temperatures above room temperature.

is attached to the anodic end, and O_2 is formed there through the membrane and another type of catalyst at the cathodic end aids in the formation of H_2 molecules, which is typically the only product considered. Although a conceptual design was presented to utilize these devices for example in the conversion of CO_2 to methanol, the design is not really functional to this objective. The Joint Center for Artificial Photosynthesis (JCAP) is the US largest research program dedicated to the development of an artificial solar-fuel generation technology. Established in 2010 as a US Department Of Energy (DOE) Energy Innovation Hub, JCAP aims to find a cost-effective method to produce fuels using only sunlight, water, and carbon dioxide as inputs. JCAP researchers are working on different components: light absorbers, catalysts, membranes, linkers, etc. The cell is based on two semiconductors as light absorbers embedded in an electron- and ion-conducting membrane. The membrane will separate the cell into two compartments, in which either the water oxidation or reduction reactions occur. JCAP has promised to deliver a working prototype of an artificial leaf by the time its initial grant runs out in 2015.

Besides, many of the alternative approaches are being pursued elsewhere. The EU project SOLIDROMICS aims to develop hybrid artificial leaves able to split water. Competing efforts are those of MIT, EPFL, Leiden University,

University of Messina, Imperial College, CALTECH, between the others. In Santa Barbara, California, for example, a start-up firm called HyperSolar is testing a system in which coated nano- or micro-particles combining a photoabsorber and a catalyst are placed in a transparent, water-filled plastic bag. The bag will inflate as it is exposed to sunlight, and hydrogen and oxygen form inside. Such units could be deployed in sunny regions such as deserts.

There are two main classes of PEC solar cells described in literature, although with some subclasses in terms of type of electrodes and specific configurations:

- a “conventional” PEC cell operating in a liquid electrolyte (aqueous concentrated electrolyte, but in principle organic or ionic liquid electrolyte could be used, when they contain enough water to drive the reaction), where water oxidation and reduction steps (to generate O_2 and H_2 , respectively) occur on the two opposite electrodes in contact with the electrolyte which mediates the reactions and closes the circuit [22];
- a “modified” PEC cell based essentially on the integration of a PV cell (single or preferably multi-junction cell to obtain the necessary potential to drive water electrolysis – 1.23 eV – plus the necessary overpotential, e.g. around 1.8 eV in total) with catalytic elements able to use the photogenerated current/potential to oxidize water to O_2

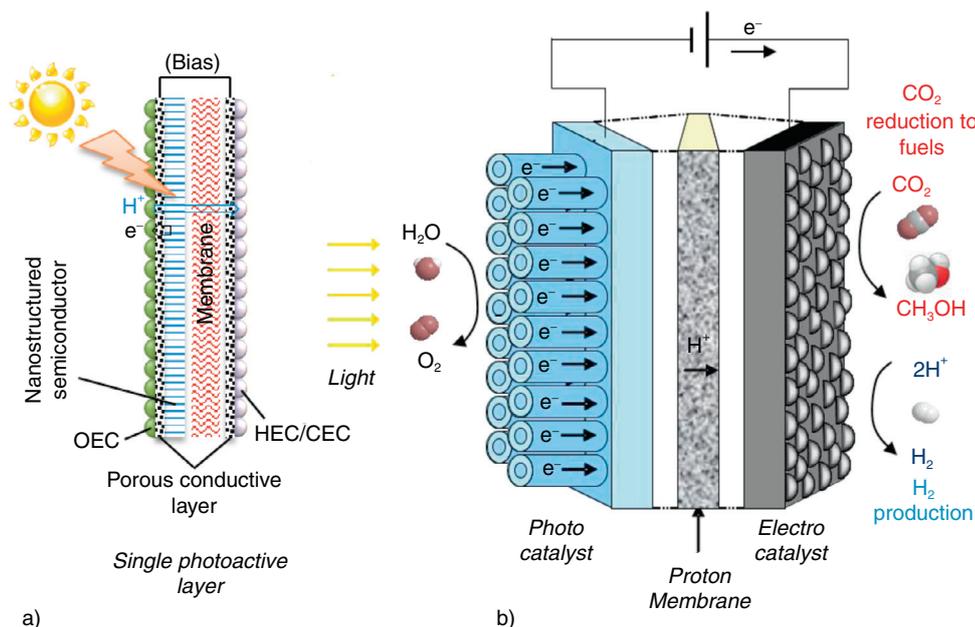


Figure 6

a) Scheme of an EL-PEC solar cell and b) realization of this type of cell at the University of Messina. Adapted from References [22, 70].

and H^+/e^- (often these elements are indicated with the acronym OEC) and reduce H^+ to H_2 on the other electrode (HEC) [30].

The temperature of operation is a critical limiting factor in both these types of cells, together with the possibility to operate efficiently in the reduction of CO_2 rather than in the evolution of H_2 . Higher temperatures of operation allow the possibility to change and optimize also the charge transport across interfacial structures, a factor often limiting efficiencies. In addition, it can enhance hot-electron transfer, significantly increasing solar-to-electric power conversion efficiencies. From a practical perspective, it is necessary to consider that under full irradiation with solar light in summer, the cell may rise temperature up to about 60-70°C in the absence of cooling. The PEC cell accounts for the largest part of the costs to produce solar fuels. To reduce these costs, it may be interesting to couple the cell with low-cost solar light concentrators such as Fresnel lens. Under these conditions, the temperature of operation of the cell may easily reach temperatures above 100-150°C. The types of cell as those commented above and typically studied in literature are not suited for operations above r.t. and the largest part of the materials for PEC solar cells are also not stable for operations above r.t.

Operations without a bulk electrolyte (electrolyte-less conditions, EL) may greatly help to develop PEC solar cells for high temperature operations [126]. Interesting

indications, on both the limiting steps of the process and the reaction mechanism, have been obtained comparing CO_2 reduction performed on the same electrodes in the presence (liquid-phase) or absence (gas-phase) of a bulk electrolyte. Another relevant motivation for the electrolyte-less operation is that recovery of the products of reaction is costly and significantly decreases the overall energy efficiency of the devices, which should include the energy cost to recover the product of reaction (an aspect typically not considered). In the absence of a bulk electrolyte and in a flow PEC cell, the products of reaction may be instead easily recovered from the gas phase outlet of the cell. Figure 6a illustrates the scheme of EL-PEC solar cell, and Figure 6b how the concept was applied (at University of Messina, Italy) to realize a practical cell able to convert selectively CO_2 to isopropanol, although with still low productivities due to the complexity of the conversion (a multi-electron reduction).

Thus, among the recent progresses in this field, a particular attention is devoted to the design and development of “artificial leaf” devices and to some of their critical components. This research area is very active with different concepts and ideas under investigation, although often the validity of proposed solutions needs to be proven and many constraints are not fully taken into account particularly from the perspective of system engineering. Addressing such challenging problem requires a complex multitasking approach because it is necessary not only that each artificial

leaf's component works well, but also combine all of them into a complete system that works efficiently. This is even harder.

CONCLUSIONS AND OUTLOOK

In this perspective, we have presented the scenario, analyzing problems and perspectives related to the various technologies under examination for solar production of fuels from water and CO₂ and tried to discern among the various options, the current most feasible and favorable ways contributing to solve the problem of future energy supply. The promising route towards the development of artificial energy systems able to directly capture CO₂ and convert it into liquid solar fuels are also discussed, evidencing the requirements requested to the artificial leaves with respect to the natural ones, such as a higher solar-to-chemical conversion efficiency, together with robustness and cost-effectiveness.

Continued support coming from fundamental research across the range of fields regarding chemical sciences will play a key role in achieving the breakthroughs that are needed to provide practical technologies to produce solar fuels. Key research areas include catalysis, photocatalytic and electrochemical properties of organic and inorganic materials, molecular mechanisms for light harvesting and transport, nanomaterials and structure and properties of surfaces.

The challenge is exciting and cannot be postponed, the stake is the future of our energy supply system and the sustainable development of our planet.

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