

A Novel Photo-electrochemical Approach for the Chemical Recycling of Carbon Dioxide to Fuels

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In this work we present the opportunity to recycle CO₂ back to liquid fuels, by using a novel PhotoElectroChemical (PEC) approach integrated with the utilization of nano-sized materials as (photo)electro-catalysts. Even if the perspective is still a long-term objective, some good advances in this direction already exist. An example is the particular PEC reactor that we have developed for H₂ production by water photoelectrolysis but that can ideally be adapted for gas phase reduction of CO₂ to fuels. The photo-reactor, working like a reverse fuel cell, was realized in a highly compact configuration in order to minimize light scattering phenomena and increase the photo-efficiency of the process. Results, obtained separately from experiments with the photoanode (H₂ production by solar light) and the electrocathode (CO₂ reduction by current application), are very promising for a future application in the chemical recycling of CO₂, as a complementary technology to carbon sequestration and storage.

1. Introduction

Carbon dioxide is one of the principal greenhouse gases that enter the atmosphere because of natural processes and human activities. The quantity of CO₂ coming from fossil fuel combustion has accounted for approximately 80% of the global warming potential weighted emissions since 1990. In order to limit the consequences due to the climate change, it is urgent to develop new technologies for greater energy saving and efficiency, and to find in a medium term a sustainable solution to CO₂ emissions. However CO₂ is recently turning image and there are increasing attempts to consider it a resource and a business opportunity rather than a waste with a cost of disposal (Centi and Perathoner, 2009). Increasing amounts of low-cost and relatively pure CO₂ will be soon available from current and planned plants for carbon sequestration and storage (CSS). Therefore, CO₂ will be a feedstock of nearly zero (or even negative) cost for conversion to fuels and chemicals, in addition to the many benefits in terms of positive image for companies, which will adopt politics of reduction of CO₂ emissions. The other factor stimulating the interest in CO₂ chemical recycling is the presence of many emissions for which the CSS option is unsuitable: distance from safe sequestration sites, diluted concentration of CO₂ in the emitting gas, small-medium size sources, and uncertainty of the environmental impact.

There are different options to convert CO_2 . In this work we focused the attention on the reduction of CO_2 to liquid fuels, by using a novel photo-electrochemical (PEC) approach. This process, carried out at room temperature and atmospheric pressure using solar light, represents a highly challenging approach to close the CO_2 cycle and develop photosynthesis mimic approaches (Ampelli et al., 2010). The core of the PEC system is a particular homemade photo-reactor, built in Plexiglas and equipped with a quartz window. It was realized in a highly compact configuration in order to minimize scattering phenomena and increase the photo-efficiency (Ampelli et al., 2009). The PEC reactor has a two-electrode configuration with two compartments and it can be used either for H_2 production by water splitting or for CO_2 reduction back to liquid fuels (hydrocarbons, alcohols with $\text{C}>2$). The photo-anode is a nanostructured TiO_2 thin film supported over a porous titanium foil (Ampelli et al., 2008). The cathode consists of Pt(or Fe)/carbon nanotubes (CNT) supported on carbon cloth (CC). The two electrodes are joint together by a protonic membrane (Nafion[®]). The simplified process can be summarized as follows: i) light crosses the quartz window and reaches the nanostructured film (photoanode) where photo-generated electron and hole pairs are generated and O_2 evolves, ii) protons pass through the protonic membrane, while electrons are collected and reach the cathode through an external wire, and iii) protons react with CO_2 in the presence of electrons on the CNT based electrocatalyst to give liquid fuels, or recombine with electrons over Pt nanoparticles supported on carbon cloth to give H_2 (see Fig. 1). The physical separation of the two reactions of water oxidation and CO_2 reduction in a photoanode and electrocathode respectively, is necessary to increase the efficiency of the process and limit charge recombination. Moreover, this device could be used to produce renewable H_2 by photocatalytic reforming of chemicals present in waste streams from agro-food or agro-chemical production, such as diluted streams of ethanol, glycerol, etc.

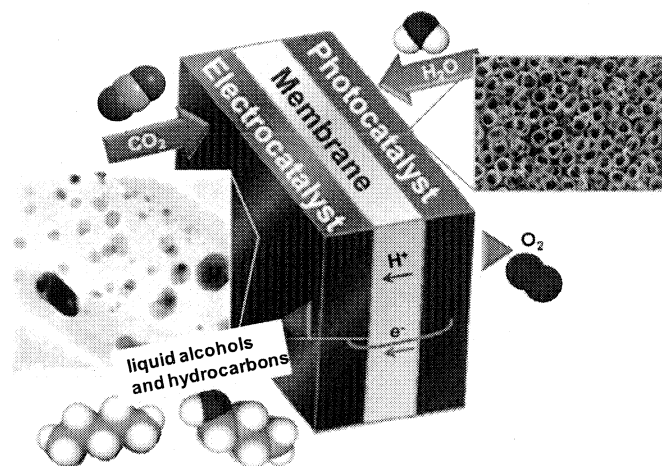


Figure 1: Simplified scheme of the PEC reactor for the CO_2 reduction to fuels using solar energy.

2. Experimental

2.1 Preparing and assembling the electrodes

TiO₂ nanotube arrays, used as photo-anodes in the PEC reactor, were synthesized by controlled anodic oxidation of Ti foils. The essence of the method may be described as a reconstruction of a thin TiO₂ layer, formed initially by oxidation of a Ti foil, which occurs under the application of a constant bias in presence of fluoride-based electrolytes (Mor et al., 2006). Details about the geometry of the cell and the procedure of preparation were described elsewhere (Ampelli et al., 2008). 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 (at least 10x10 cm). The electrocathode instead was prepared by depositing a suspension of Fe/ or Pt/CNT in ethanol on carbon cloth (CC), with a final metal loading of ~0.5 mg/cm². Commercial CNT (supplied from Applied Science Inc., XT24PS), used as starting materials, were initially treated: i) in inert gas at 700°C, in order to remove the amorphous carbon present on the outer surface and reduce the number of structural defects, thus increasing the graphitic character of the CNT; ii) in nitric acid under reflux (HNO₃ 65%) at 100°C for 10 h to create oxygen functional groups on the surface of the CNTs, which are necessary to better anchor the metal particles. Then, the CNTs were impregnated with 10 wt % Fe or Pt using Fe(NO₃)₃·9H₂O or H₂PtCl₆ as precursors, annealed for 2 h at 350°C, reduced under H₂ flow at 400°C for 2 h and deposited on CC. The electro-cathode operates in contact with i) CO₂ in gas phase (or inert gas in the case of H₂ production), ii) the protons (provided by the opposite side of the PEC reactor which diffuse to the electrocatalyst through a Nafion[®] membrane) and iii) the electrons (provided by the external circuit and generated on the TiO₂ photo-anode). The two electrode layers (nano-structured TiO₂ photo-catalyst and Fe/ or Pt/CNT on CC electrocatalyst) were assembled together with the Nafion membrane by hot pressing at 120°C under a pressure of 20 kg cm⁻², so to create a membrane and electrode assembly (MEA) very similar to those used in fuel cell technology. The adherence between the two electrode layers and the Nafion[®] membrane is very important to attain a good electrical insulation and proton transport.

3. Results and discussion

The electrocatalytic reduction of CO₂ to fuels may be sustainable only when the electrons and protons necessary for the reaction are supplied using renewable resources, e.g. by solar energy. The integration of a photoanode hemi-cell, able to harvest efficiently solar light and produce protons and electrons by oxidizing the water (with production of O₂), and an electrocathode hemi-cell, where protons and electrons combine together with CO₂ giving liquid fuels (oxygenates and hydrocarbons with C>2), is a good solution toward this direction of energy sustainability. Referring to photoelectrochemical (PEC) devices, the efforts of scientists are focalized on two different routes. On the one hand it is necessary to improve the electrode materials. The photoanode must be able to absorb light particularly in the visible region, since UV

radiation is only a small part of the solar spectrum (~4%) and TiO₂ materials show a too high band gap (3.2 eV) for a real application under solar irradiation. The photoresponse with visible light may be enhanced by doping or decorating TiO₂ with metal particles. Moreover the ability to synthesize and control the nano-architecture allows to realize a confined environment suited for the deposition of metal nano-particles (inside or outside the TiO₂ nanotubes) which may diminish the band gap and consequently improve the absorption of the visible part of the light irradiation. The electrocathode must be able to provide a high absorption of CO₂ and good collection of protons and electrons coming from the photoanode. Both the electrodes must be in the form of thin films, to be pressed like a MEA in fuel cells, taking effective advantage of the large technological developments made on these systems in the recent years. On the other hand it is necessary to concentrate efforts on the design of the PEC reactor, because the photo-efficiency of the process also depends strongly on the geometrical configuration of the reactor, particularly on the optical path of the light within the reactor, in order to attain the maximum benefit from the pattern of irradiation. 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. We here discuss results obtained separately by experiments with the electrocathode and photoanode in CO₂ reduction to fuels and H₂ photoproduction processes respectively.

3.1 Electrocatalytic reduction of CO₂ back to liquid fuels

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 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 CNT, 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 (Fig. 2).

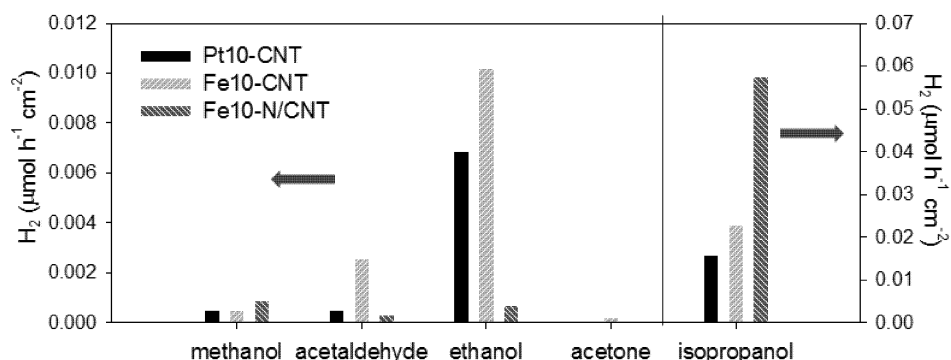


Figure 2: Product distribution at 60°C in the electrocatalytic reduction of CO₂ in the gas phase over Nafion® 117/(Pt or Fe_(10%)/CNT)_{20%}/carbon cloth GDM (gas diffusion membrane) electrode.

3.2 Photo-production of H₂

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 the proton-conductor membrane. The use of a specific nanostructure in the photoanode may improve the light harvesting and limit the 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 easily scalable to large films. The nanostructured titania thin films may be used in either liquid or gas phase, particularly for the case of H₂ production by photoreforming. Table 1 reports the comparison of the rates of H₂ production during ethanol–water photoreforming in liquid phase (room temperature) and in gas phase (70°C). It is evident that in gas phase, due to the reduced light scattering by the water and more efficient desorption of the adsorbed species which quench the photoinduced processes, the rate of H₂ production is one order of magnitude higher than in liquid phase. Gas phase photoreactions in H₂ production are a rather unexplored area, but these results indicate a quite promising area to investigate. Table 1 also evidences the role of the presence and nature of Pt nanoparticles on titania in increasing the rate of H₂ formation. The addition of 0.5 wt % Pt to titania 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.

Table 1: Rate of H₂ production for nanostructured TiO₂ thin films with or without Pt and under liquid or gas phase conditions, during photoreforming of 10% ethanol in water. Temperature: liquid phase 40°C; gas phase 70°C (temperature of the evaporating solution).

Type of experiment	Hydrogen ($\mu\text{mol h}^{-1}$)
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

4. Conclusions

The results of this work evidence that using Pt(or Fe)/CNT electrocatalysts it is possible to convert CO₂ to liquid fuels, particularly isopropanol. This is the first time, to our knowledge, that it is demonstrated that this difficult and challenging reaction (a 18 electron conversion) could be realized with reasonable productivities. Fe/CNT show a better behavior than Pt/CNT, although a faster deactivation which, however, occurs in both cases after few cycles of reaction. Preliminary tests not reported here, however indicate that Fe–Co/CNT samples show an even more stable behavior. These processes are only at an early stage, but with relevant potential in the future, if electrons and protons necessary for CO₂ reduction will come from sustainable resources, such as solar energy and water. In a long term, the photoelectrocatalytic reduction of CO₂ under solar irradiation together with other new potential technologies (i.e. thermal CO₂ reduction), could greatly increase carbon recycling and reduce the fossil fuel consumption.

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