

A Gas-phase Electrochemical Reactor for Carbon Dioxide Reduction back to Liquid Fuels

Chiara Genovese*, Claudio Ampelli, Siglinda Perathoner, Gabriele Centi

Department of Electronic Engineering, Industrial Chemistry and Engineering, University of Messina
 Viale F. Stagno D'Alcontres, 31 - 98166 Messina (Italy)
 cgenovese@unime.it

We discussed here on a novel approach to recycle CO₂ back to liquid fuels by using nanostructured carbon-based materials (doped with suitable metal nanoparticles) as electrocatalysts. This approach is based on the development of a new photo-electrocatalytic (PEC) reactor, working in gas phase, which is quite different from the conventional reactors that operate typically in aqueous slurry and/or in batch. Gas phase operation, under solvent-less conditions, has many advantages (easy recovery of the products, no problems of CO₂ solubility, etc.) with respect to liquid phase. The reaction mechanism is also quite different and longer chains of products can be obtained. In particular we investigated the competition of the side reaction of H₂ formation by water electrolysis (which is unavoidable in such kinds of systems) with the CO₂ reduction process. The understanding of this competitive reaction is very significant in order to maximize the process performances. Moreover the capability to develop advanced nanostructured electrodes, by modulating their properties during the synthesis, allowed to improve the efficiency of the CO₂ reduction process, enhancing the productivity and tuning the selectivity towards higher chain hydrocarbons and other chemicals. The CO₂ reduction to liquid fuels by solar energy represents an attractive solution which may contribute to the alternative use of clean and renewable sources to cope with the depletion of fossil fuels. The target is to develop a sort of "artificial leaf" which may collect the solar energy as the nature does, by capturing directly CO₂ and converting it back to fuels.

1. Introduction

The need of finding new solutions for a clean and sustainable energy is becoming a critical factor for the future of society (Kathoch and Bhat, 2010). There is a progressive depletion of fossil fuels and their use is made difficult by economic and environmental matters (Centi et al., 2011). It is so necessary to find alternative feedstocks to fossil fuels and develop innovative routes to close the CO₂ cycle. In this framework the possibility to catalytically convert CO₂ has recently received considerable attention because it may produce valuable chemicals starting from an useless compound as carbon dioxide. Increasing amounts of low-cost and relatively pure CO₂ will be soon available from current and planned plants for carbon sequestration and storage (CSS) (Centi and Perathoner, 2009).

In the last years, different kinds of devices have been developed for converting solar energy into chemicals with the attempt to mimic the natural photosynthesis processes (Bensaid et al., 2012). The research goals are centred to the need to develop not just efficient, but also cost-effective and robust technologies and materials to be used in solar energy applications. The process of CO₂ reduction to liquid fuels is considered as one of the artificial photosynthesis processes. Photosynthesis by plants, as known, consists of two main reactions: in the light reaction the water is decomposed to H₂ and O₂ under sunlight irradiation and in the dark reaction adsorbed CO₂ is hydrogenated by H₂ and fixed as carbohydrates. To mimic what plants do during the natural photosynthesis, the artificial devices should be designed to reduce CO₂, but it is a common practice to consider artificial photosynthesis as a simplified process of using sunlight to break water into H₂ and O₂ (Hoffmann et al., 2011).

Our approach is based on a novel photo-electrocatalytic (PEC) reactor working in gas phase (Ampelli et al., 2012a) which consists of: i) a photo-anode formed by a TiO₂ thin film characterized by a highly ordered

nanostructure where O_2 , protons and electrons are produced by water splitting (Passalacqua et al., 2012); ii) an electro-cathode composed of metal nanoparticles supported on C-based substrates with a configuration similar to a gas-diffusion membrane (GDM), in which CO_2 is reduced using the protons and electrons coming from the anode side and passing through a proton selective membrane (Nafion[®]) and a wire, respectively (Ampelli et al., 2011a). The design of the PEC reactor takes advantage of fuel cell technology and the electrode materials are assembled together like a MEA (membrane electrode assembly) in a fuel cell (Ampelli et al., 2009).

Gas phase operation is very attractive because allows to solve some critical issues related to aqueous slurry reactors, which are used in the most of the electrocatalytic processes of CO_2 reduction reported in literature (Varghese et al., 2009): there is no solvent at the cathode side and therefore no need to recover the products from a liquid phase, no problems of CO_2 solubility, etc. Moreover in gas phase the reaction mechanism is quite different and longer chains of products may be obtained; in the liquid phase instead the main products obtained are C1 (or at most C2) hydrocarbons or oxygenates. The target is in fact the formation of liquid fuels with $C \geq 2$ because they are easier to transport and store, preserving the large investments made in the current energy and chemical infrastructures (Ampelli et al., 2011b). Therefore, CO_2 electrocatalytic conversion has the potential to become a key pillar of the sustainable and resource-efficient production of chemicals and energy from renewables.

The aim of this work is to investigate the feasibility of the electrocatalytic gas-phase conversion of CO_2 to hydrocarbons and oxygenates using C-based nanostructured electrocatalysts (doped with Pt and also with not noble metal nanoparticles, i.e. Fe) as part of a photoelectrocatalytic (PEC) device which, by using sunlight and water, is able to convert CO_2 back to liquid fuels (Ampelli et al., 2010). The nature of the electrocatalyst plays a significant role to control the process yield and selectivity allowing to form long C-chain liquid fuels. We started from commercial carbon nanotubes (CNT) and then modified them by using advanced chemical and thermal techniques. The CNT are suitable materials to prepare such kinds of electrodes for their high electron conductivity, flexibility and possibility of easy tuning of properties during the synthesis (Centi and Perathoner, 2011). The influence of: the kind of CNT, deposition of metal nanoparticles, different operating conditions and various other aspects were evaluated in order to improve the productivity and selectivity.

In particular, the mechanism of H_2 formation as side reaction in the electrocatalytic process was in depth investigated. This aspect has poorly been studied in literature but is of paramount importance to enhance the overall process efficiency.

2. Experimental

Commercial multiwalled carbon nanotubes with inner diameter in the range of 50–100 nm were purchased from Applied Science (CNT, Pyrograph[®]-III, PR24) and used as starting materials. The CNT were heat-treated in inert gas at 700 °C (PS), 1500 °C (LHT) or 3000 °C (HHT) to remove the polyaromatic carbon layer covering their outer surface thus increasing the graphitization level and inherent conductivity. Then the samples were chemically treated in boiling nitric acid (HNO_3 65 wt. %) for 10 h to functionalise the surface of the CNT creating a variety of oxygen groups. Finally they were washed with distilled water until neutral pH and dried at 80 °C overnight. 10 wt. % Fe or Pt were deposited on CNT by incipient wetness impregnation using as precursors $Fe(NO_3)_3 \cdot 9H_2O$ or H_2PtCl_6 solutions, respectively. After drying at 60 °C for 24 h, the samples were annealed for 2 h at 350 °C and reduced in H_2 at 400 °C for 2 h.

The electrodes were prepared by using methods which are easy, cost-effective and potentially scalable for a large use but an appropriate assembly of the electrode materials is fundamental for a good contact and adherence of the different layers. The electrodes are in the form of a gas diffusion membrane (GDM) consisting of a gas diffusion layer (GDL) and a Nafion[®] membrane, which are assembled together to allow the electrical contact and diffusion of gas phase to the electrocatalyst. To prepare the GDL, an ethanol suspension of metal-doped CNT was deposited on a commercial substrate (SIGRACET[®] GDL 24BC, supplied by SGL Group) with a final metal loading of about 0.5 mg cm^{-2} . After drying, the final GDM working electrode was assembled by hot-pressing joining the GDL on a proton selective membrane (Nafion[®] 115, by Sigma Aldrich) at 80 atm and 130 °C for 90 s. The active phase (CNT) is located between the GDL at direct contact with CO_2 gaseous stream and the Nafion[®] membrane. A 1 cm^2 electrode was used.

The experiments were carried out in a homemade continuous hemi-cell at 60 °C and for simplicity the photo-generated current was simulated by applying a constant small bias through the cell to supply the electrons necessary for the CO_2 reduction process. In this configuration the photo-anode was replaced by a compartment filled with a liquid electrolyte solution as source of protons; a Pt wire (as counter-electrode) and a saturated Ag/AgCl electrode (as reference electrode) were located in this part of the reactor. In the

final PEC system, no electric potential and electrolyte will be needed, as the protons and electrons will be produced by water photo-electrolysis (activated by solar light).

A potentiostat/galvanostat (Amel mod. 2049A) is used to supply the current and monitor the potential between the working and counter/reference electrodes. Experiments were conducted galvanostatically, inverting after 1 h the current polarity to improve desorption of the products from the working electrode. The analysis of the products of the reaction, collected in a cold trap, was performed by a gas-chromatograph equipped with a mass detector (Thermo Scientific GC Trace 1310 - ISQ MS).

3. Results and discussion

The gas phase reduction of CO₂ to liquid fuels is a complex multistep reaction involving shared intermediates and multiple reaction pathways and the mechanism is probably quite different in comparison with the liquid phase conditions in which mainly C1 products are obtained.

The key aspect in order to improve the overall efficiency is not only the preparation of a proper C-based nanostructured electrode (doped with suitable metals) but also the capability to assemble the electrode materials to form a multilayered composite to guarantee good proton mobility and electron conductivity. The reactor was in fact designed taking into account these engineering aspects which are usually the critical factors limiting these kinds of cells.

Another important issue, poorly investigated, in such a kind of electrocatalytic cell configuration is the presence of water which is in both the hemi-cells. The process, in fact, consists of two half-reactions which, for simplicity, we report only for the production of isopropanol, as follows:



Water is present at the anode side (photo-anode or simulated-anode in our current PEC system) where it is oxidized to give O₂ (Eq. 1) while protons and electrons migrate to the other side through the Nafion® membrane and the external circuit, respectively. At the cathode side protons and electrons combine together with CO₂ to form fuels and water (Eq. 2). Moreover, a small amount of water arrives at the cathode side through the Nafion® membrane (due to its permeability) because it is in direct contact with the anode aqueous solution. Thus, the presence of H₂O in the electrocatalytic system is unavoidable. Unfortunately the standard reduction potential of H₂O to form H₂ is considerably lower than the standard reduction potential of CO₂ to form CO₂^{•-} (Indrakanti et al., 2009). Therefore, from a thermodynamic point of view it should generally be more favourable to reduce H₂O than CO₂, but so far this aspect has still not been investigated. In order to minimize the competitive side reaction of water splitting, we analysed the outlet gas phase stream from the reactor to determine the H₂ generation rate.

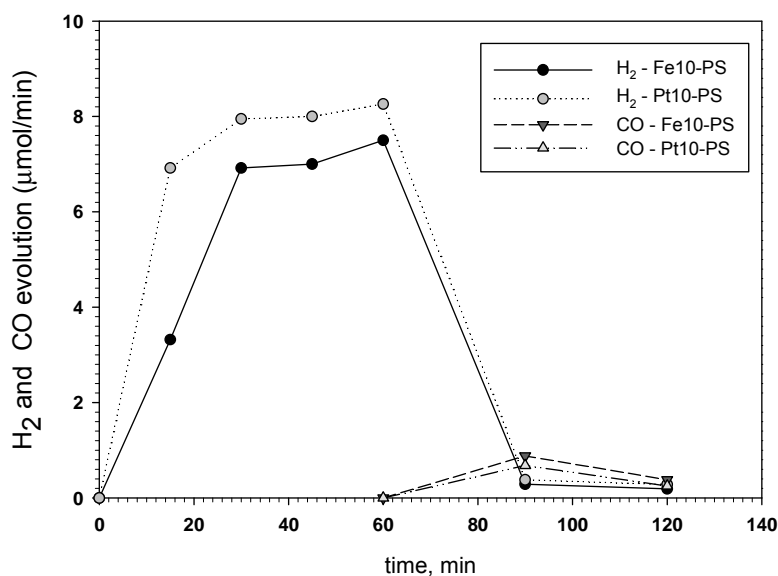


Figure 1: H₂ and CO production rates for Fe/CNT and Pt/CNT electrocatalysts treated at 700 °C (PS) (The amount of metal is 10 wt.%)

Generally the deposition of noble metal nanoparticles, and particularly Pt, plays a beneficial effect on the efficiency of a water splitting process. It has been found that the presence of small size Pt particles (5-10 nm) facilitates the kinetics of H₂ formation which desorbs to the gas phase, because the Pt nanoparticles act as electron attractors and sites of proton adsorption/desorption (Ampelli et al., 2012b). Although with some differences (i.e. photo-catalytic processes of water dissociation are catalysed by semiconductors, usually titania) the deposition of 10 % Pt nanoparticles on CNT (sample Pt10-PS) increased H₂ generation with respect to not noble metal (Fe10-PS) as it is shown in Figure 1. On the contrary, carbon monoxide, which is the main intermediate in liquid fuel generation, was produced in higher concentrations for Fe than Pt. It is to notice that during the first step of the electrocatalytic process (1 h), no CO was detected in the outlet gas stream, probably because it remains chemisorbed on the surface of the electrocatalyst. The inversion of the applied current facilitates the desorption of CO, which was thus detected in the outlet gas stream (Figure 1), as well as of the liquid fuels which were collected in the cold trap.

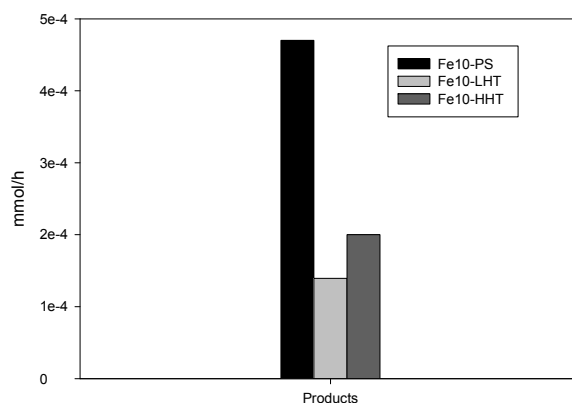
Another aspect to take into account is the power supply to be furnished in order to simulate the solar energy. The quantity of the electric current depends not only on the efficiency of the electrocatalyst but also on the reactor design. In fact, to perform a (photo)electrochemical process a power (or sunlight) supply is needed to make the process thermodynamically favourable, but also the sovrapotential effects should be taken into account and these phenomena strongly depend on the reactor configuration and electrode assembling. Initially we measured an average open circuit potential of ~0.6 V; thus the current to be furnished to the simulated PEC system was at least 10 mA (due to the ohmic losses of the cell). We performed also testing experiments at 20 mA and results are summarized in Table 1 for both Pt and Fe on CNT (PS).

Table 1: Productivity for Fe/CNT and Pt/CNT electrocatalysts treated at 700 °C (PS)

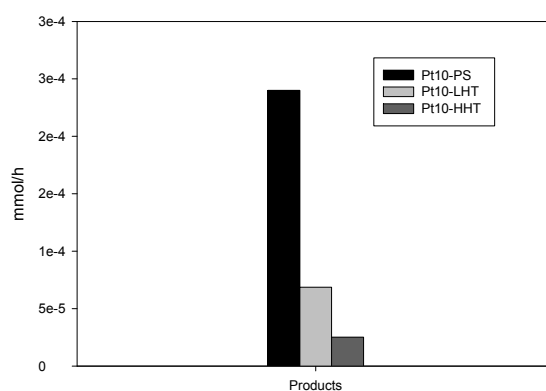
	10 mA			20 mA		
	Products (mmol/h)	H ₂ (mmol/h)	CO (mmol/h)	Products (mmol/h)	H ₂ (mmol/h)	CO (mmol/h)
Fe10-PS	2.1x10 ⁻⁴	0.149	0.0350	4.7x10 ⁻⁴	0.320	0.038
Pt10-PS	1.6x10 ⁻⁴	0.165	0.0180	2.4x10 ⁻⁴	0.340	0.028

The electric current furnished to the system was almost totally converted into chemical energy (with conversion higher than 90 %). There is a good agreement of the productivity data (total amount of liquid products and hydrogen) and a linear increase from 10 to 20 mA was observed, with the exception of carbon monoxide which remains almost as constant, especially in the case of Fe. Referring to the reaction mechanism, a possible explanation is that probably the formation of C-C bonds is the rate determining step of the whole CO₂ reduction process, but more specific investigations are needed to confirm this hypothesis. Other experiments were performed increasing the applied current to the cell above 20 mA (until 40 mA) and a worsening of the productivity was observed, although slightly increasing the fraction of heavier products (≥C₂). It is to notice that higher chain hydrocarbons (C₃-C₈) were detected in all the testing experiments, but here we have limited our analysis to the fractions C₁-C₃ which we were able to identify unequivocally (methanol, ethanol, acetaldehyde, isopropanol, acetone, acetic acid, etc.).

Furthermore, the nature of carbon-based substrate influences the catalytic efficiency; for example the presence of different surface functional groups that better anchor the metal nanoparticles (which are the actual catalytic sites) may strongly modify the intrinsic reactivity of CNT (Su et al., 2012). Also the heat-treatment is very useful to remove the polyaromatic carbon layer covering the outer surface of CNT and increase the graphitization level and inherent conductivity. In order to investigate this aspect, preliminary experiments were carried out comparing the CNT samples thermally treated at different temperatures (PS, LHT and HHT). The CNT contain the same loading of Fe or Pt (about 10 wt. % with respect to CNT, ~0.5 mg/cm² of the electrode surface). Figure 2 shows results of experiments for Fe and Pt electrocatalysts on different CNT. It is evident that CNT-PS samples give the best performances in CO₂ reduction process in terms of hydrocarbon and oxygenate productivity.



(a)



(b)

Figure 2: Productivity for Fe/CNT (a) and Pt/CNT (b) electrocatalysts treated at 700 °C (PS), 1500 °C (LHT) and 3000 °C (HHT). (The amount of metal is 10 wt. %)

Thus the increase of graphitization of the external surface of CNT by annealing at higher temperatures (from 700 up to 3000 °C) produces worse results, because probably it is more difficult the functionalization by chemical treatment, and consequently the efficient dispersion of metals to produce small particles (Gangeri et al., 2009). Evidently the presence of defects on the C-based substrate, that act as anchoring sites for the stabilization of the metal nanoparticles, is of great importance to perform the electrocatalytic process and 700 °C was the optimal temperature to guarantee both a good level of graphitization (high electron conductivity) and the right presence of defects. For this reason, we preferred to carry out all the experimental tests (previously reported) by using CNT-PS samples (treated at 700 °C) as C-based support.

4. Conclusions

In this work we developed a novel (photo-)electrochemical device for the CO₂ reduction back to liquid fuels working in gas phase and we optimized the electro-cathode part by using C-based materials doped with Fe or Pt nanoparticles. The CNT are very suited to develop advanced nano-structured electrodes, for the realization of solar devices which may mimic the natural photosynthesis.

Many different aspects influence the process of CO₂ reduction: i) the need to have a good mobility of both the electrons and active hydrogen species on the metal nanoparticles, ii) the efficient contact with the proton selective membrane and iii) the possibility of introducing specific active sites in CNT.

In particular we discussed on the competitive reaction of H₂ generation by water electrolysis, which has to be minimized. Unfortunately, the presence of water is unavoidable as it is a co-product of the cathode half-reaction and also permeates through the Nafion® membrane, but the use of Fe instead of Pt allowed to reduce the H₂ formation enhancing the productivity of liquid fuels. Experiments at different power supply (10-20 mA) gave us information about the reaction mechanism. The formation of C-C bonds is probably

the rate determining step of the whole CO₂ reduction process, but more specific investigations are needed to confirm this hypothesis. Moreover, a study on the nature of reaction intermediates could further improve the understanding of the mechanism which is probably quite different in gas than liquid phase. It may resemble a Fischer-Tropsch reaction but the operating conditions are quite different, i.e. the process occurs at lower temperatures (60 °C).

The electrocatalyst was designed to be finally coupled, in a PEC cell, to a photo-active material (based on TiO₂) which is able to absorb efficiently sunlight and convert it into chemical energy (Ampelli et al., 2008). The actual implementation of a solar PEC cell is still a long way off and both the electro- and photo-materials must be improved in terms of performance, robustness and cost. All these aspects may take advantages of the large diffusion of PEM fuel cells, since they show several analogies with PEC cells. Therefore, although there will be necessary a long time of research before a real application, the possibility to develop a PEC device able to convert CO₂, water and sunlight back to liquid fuels by using not expensive materials, is now an attractive prospective but placed on real basis.

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