

An Electrochemical Reactor for the CO₂ Reduction in Gas Phase by Using Conductive Polymer Based Electrocatalysts

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We discussed here on a novel approach to reduce CO₂ back to liquid fuels by using an electrochemical device working in gas phase. Operating under solvent-less conditions is very attractive and has many advantages with respect to a slurry reactor working in liquid phase: easier recovery of the products, no problems of CO₂ solubility, different reaction mechanism favouring C-C bond formation and producing longer chains of products. The materials used as electrocatalysts consist of conjugated microporous polymers (TPE-CMP) doped with Pt nanoparticles (acting as active phase) and mixed with carbon nanotubes (CNT) to guarantee a high electronic conductivity. The presence of the polymer may strongly enhance CO₂ absorption due to its pore structure which is completely π -conjugated. The electrocatalytic composite materials were fully characterized and tested in the electrocatalytic process of CO₂ conversion in gas phase. The catalytic experiments were performed by using a homemade electrochemical cell with three-electrode configuration. The two compartments are separated by a membrane electrode assembly (MEA) consisting of a proton conductive membrane in contact with a gas diffusion layer. The active composite material was located between these two layers. Results showed good performances in terms of liquid product formation (methanol, ethanol, acetone, isopropanol, etc.) due to the high local concentration of CO₂ on the polymer surface where the active metal nanoparticles are deposited. The results are very promising and open new possibilities in the electrocatalytic conversion of CO₂ to liquid fuels by exploiting solar energy and closing the CO₂ cycle of its production/consumption.

1. Introduction

Interests in carbon dioxide and its conversion to solar fuels have recently been grown for the new idea of CO₂ as a future source of energy and carbon to face the depletion of fossil fuels and reduce the greenhouse gas emissions (Genovese et al., 2013a). There is a general agreement that the future energy scenario will be based on an increasing use of clean and renewable sources (Schlögl, 2012). Unfortunately, these kinds of energy sources are characterized by a discontinuous production, which implies the need to change to a model of smart grids where the match between production and use is realized through devices which may store renewable energy (Ampelli et al., 2014a). The conversion to chemical energy is still the preferable option to realize high energy density and low cost storage devices, particularly when liquid fuels are the result of this energy conversion process (Ampelli et al., 2012). Liquid fuels are also well suited for the transport to long distance of energy, an important element for a more rational use of renewable energy sources on a global scale (Newman et al., 2012). Conversion of CO₂ to chemicals is an enabling factor for this vision, because the products of this conversion (in particular, methanol and longer C-chain hydrocarbons and alcohols) perfectly integrate within the current energy infrastructure (Ampelli et al., 2013). This is an important element for sustainability, because limiting the investments related to the

transition to a new energy infrastructure is a key for a fast introduction of renewable energy into the production chain. The production of solar fuels by closing the CO₂ cycle will be possible whereas i) new catalytic composite materials (able to absorb and convert CO₂ to fuels, also favouring the formation of C-C bonds) and ii) novel electrochemical devices (designed on purpose to maximize the catalytic activity) are both developed (Ampelli et al., 2011).

The possibility to combine capture and conversion of CO₂ is an attractive strategy for the reduction of carbon dioxide. In the last years, different materials able to absorb efficiently CO₂ have been developed: zeolites, alumina, metal organic framework (MOF) (Yang et al., 2012), covalent organic framework (COF) (Xie et al., 2013) and porous aromatic framework (PAF) (Ben and Qiu, 2013; Fraccarollo et al., 2014). Recently, increasing attention has been turned to a new class of organic porous materials called conjugated microporous materials (CMP) for their own characteristics, such as the intrinsic and unique combination of nanopores and π -conjugated skeleton (Xu et al., 2011). These materials are very interesting because it is possible to modulate easily their specific properties and characteristics by changing the synthetic method and/or the building blocks (Xu et al., 2013). Due to their own microporosity coupled with the high surface area, CMP have largely been investigated for gas adsorption and storage purposes. The same materials proposed for CO₂ capture seem to be the ideal candidates as CO₂ activation catalysts and substrates able to coordinate noble (Pt) and non-noble-type transition metals (Co, Fe, Cu) for a selective multielectron reduction of CO₂.

The use of these materials in the reduction of CO₂ is a new area of development and there are only a few references in literature about their use as electrodes (Dawson et al., 2011; Demir-Cakan et al., 2011). The proper assembly of a multifunctional electrode (comprising a conductive substrate, an adsorbent support and the dispersed active sites) is of great and challenging importance to increase the productivity, efficiency and selectivity of the electrocatalytic CO₂ conversion process.

In this context, we have analyzed the feasibility of the electrocatalytic conversion of CO₂ to oxygenates under gas-phase conditions, by using new conjugated microporous polymers as electrocatalysts (doped with Pt). We have tested their performances by using a homemade electrocatalytic cell, built in Plexiglas, by supplying controlled electric current and protons to the electrocathode.

2. The photo-electrochemical (PEC) cell

Recently, several studies have been focused on the question of converting CO₂ to fuels (Genovese et al., 2013b). There are various possible routes, from photocatalytic to thermochemical approaches. The current possible approach is based on a multistep sequence of producing electrical energy using renewable energy sources (solar, wind, hydropower, etc.), then producing H₂ by electrolysis and finally using this hydrogen to produce chemical and fuels from CO₂. In a longer term vision, however, it is necessary to integrate all these steps in a single photoelectrocatalytic (PEC) device able to use directly sunlight and convert the captured CO₂ and H₂O to fuels such as methanol, methane and/or >C1 hydrocarbons and alcohols. The PEC concept is based on the separation (with a membrane) of the photoelectrode for water oxidation (forming O₂, protons and electrons) and the electrode for electro-catalytic reduction of CO₂ using the protons/electrons generated at the photoelectrode (Ampelli et al., 2008). The separation of the two elements of the solar cell is necessary to avoid quenching phenomena between the reactive species and for safety aspects, related to the production of O₂ and fuels at the same place (Ampelli et al., 2009). Another important aspect to consider is the recovery of the products of reaction. Conventional PEC devices operate in liquid phase, and most of the photo- and electro-chemical studies were performed in liquid phase (Kuhl et al., 2012). However, the recovery of the products of reaction is often an energetically-costly operation which may eventually require more energy than the amount of renewable energy store in the product of reaction. For this reason it is important that the solar PEC cell design includes the possibility for an easy recovery of the reaction products, for example operating the electrocatalytic reduction of CO₂ in a cell designed for gas phase and continuous operations and suitable for easy industrial scale-up (Ampelli et al., 2014b). The electrodes for this type of operation are also conceptually different from those used in the liquid phase for CO₂ conversion. We used electrodes analogous to gas diffusion membrane (GDM) electrodes for proton exchange membrane (PEM) fuel cells, but with a different electrocatalyst, based upon metal nanoparticles on polymer-based materials which are able to convert CO₂ to >C1 alcohols and hydrocarbons.

3. Experimental

3.1 Preparation of the electrocatalysts

TPE-CMP was synthesized using the Yamamoto coupling following the procedure reported by Xu et al. (2013). In particular, 1,5-cyclooctadiene (COD, 1.05 mL, 8.32 mmol) was added to a solution of bis(1,5-cyclooctadiene)nickel(0) ($\text{Ni}(\text{cod})_2$, 2.25 g, 8.18 mmol) and 2,2'-bipyridyl (1.28 g, 8.18 mmol) in anhydrous DMF (120 mL) and the mixture was heated under Ar at 353 K for 1 h. 1,1,2,2-Tetrakis(4-bromophenyl)ethene (TBPE) (1 g, 1.54 mmol) was added to the resulting purple solution and the mixture was stirred at 353 K overnight to obtain a deep purple suspension. After cooling to room temperature, concentrated HCl was added to the mixture. After filtration, the residue was washed with H_2O (5 x 30 mL), THF (5 x 30 mL) and CHCl_3 (5 x 30 mL) and dried in vacuum to give a yellow powder (90% yield). Figure 1 shows a schematic representation of TPE-CMP formation.

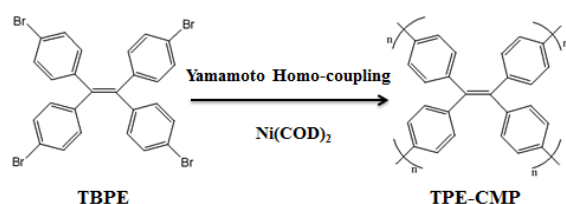


Figure 1: Schematic representation of TPE-CMP formation.

Then, 10 wt% Pt were deposited on TPE-CMP by sol immobilization technique (Wang et al., 2006) using $\text{K}_2\text{PtCl}_4 \cdot 2\text{H}_2\text{O}$ as precursor, NaBH_4 as reducer and PVA as protective agent. Then, the solution (after acidification at pH=2) was added to the support under vigorous stirring. The powder was filtered, washed until neutral pH and finally dried at 80 °C for 4 h. Platinum was deposited on CNT by incipient wetness impregnation using an ethanolic solution containing the metal precursor. 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 total amount of metals is 10 wt. %.

3.2 Characterization of the electrocatalysts

The electrocatalytic materials were fully characterized using different techniques. The Infrared (IR) spectra of the materials in KBr pellets were collected using a Bruker Equinox 55 Spectrometer equipped with a pyroelectric detector (DTGS type) with a resolution of 4 cm^{-1} . The Thermogravimetric analysis (TGA) was performed on a Setaram SETSYS Evolution instrument under argon (gas flow 20 mL/min), heating the samples up to 1373 K with a rate of 2 K min^{-1} . Transmission Electron Microscopy (TEM) images were acquired by using a Philips CM12 microscope (resolution 0.2 nm) with an accelerating voltage of 120 kV.

3.3 Assembling and testing of the electrodes

An ethanol suspension of metal-doped TPE-CMP was deposited on a commercial gas diffusion layer (SIGRACET GDL 24BC, supplied by SGL Group) with a final metal loading of about 0.5 mg cm^{-2} . The TPE-CMP doped with Pt nanoparticles were first mixed with a little amount of carbon nanotubes to increase the conductivity. Commercial multiwalled carbon nanotubes purchased from Applied Science (CNT, Pyrograph®-III, PR24) were used for this purpose.

The electrodes are in the form of a gas diffusion membrane (GDM) consisting of the GDL and a Nafion® membrane (Nafion® 115, by Sigma Aldrich), assembled by hot-pressing at 80 atm and 130 °C for 90 s. The active composite material was located between these two layers. A 1 cm^2 electrode was used.

Tests of CO_2 reduction were performed by using a homemade semi-continuous electrochemical cell with three-electrode configuration. The cell was described elsewhere (Genovese et al., 2013c). The experiments were carried out at 60 °C and the photo-generated current was simulated by applying a constant small bias through the cell to provide the electrons necessary for the CO_2 reduction process. The photo-anode was replaced by a compartment filled with a liquid electrolyte solution as source of protons (KHCO_3 0.5M). Experiments were conducted in galvanostatic mode, 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).

4. Results and discussion

4.1 Catalyst Characterization

Infrared spectroscopy was used to study the structure of the electrocatalytic materials. The IR spectra of the starting polymer TPE-CMP is reported in the Figure 2. In the low frequency region, bands with different intensities corresponding to the absorption characteristic of aromatic rings are present. The bands at 1491 and 1444 cm^{-1} involve “semicircle stretching pair” modes of the aromatic rings. The intense and sharp band at 1004 cm^{-1} is assigned to the C-C bending of the aromatic rings coupled with C-H bending. The absorption bands at 824 and 800 cm^{-1} are assignable to the ring and C-H out of plane bending.

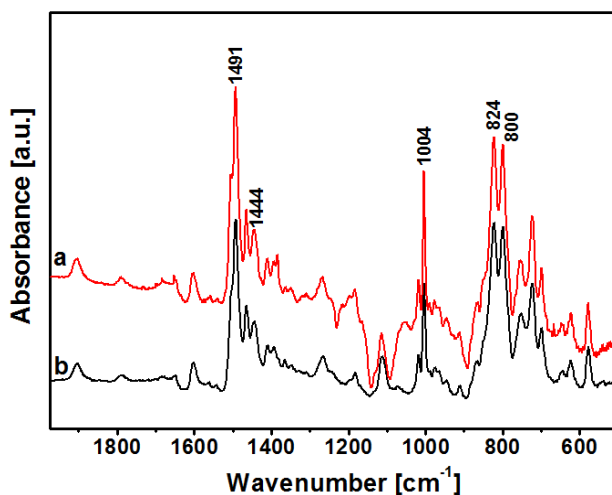


Figure 2: IR spectra in the region 2000-500 cm^{-1} of a) TPE-CMP in KBr pellet and b) electrocatalyst material in KBr pellet.

Comparing the polymer TPE-CMP (profile a in Figure 2) and the catalyst (profile b in Figure 2) it can be seen that the structural vibrational modes of the starting material have not undergone any modification, even after the sol immobilization treatment and the subsequent annealing. Thermogravimetric Analysis (TGA) confirmed the good thermal stability of the electrocatalytic material and its high temperature of decomposition above 400°C, as shown in Figure 3.

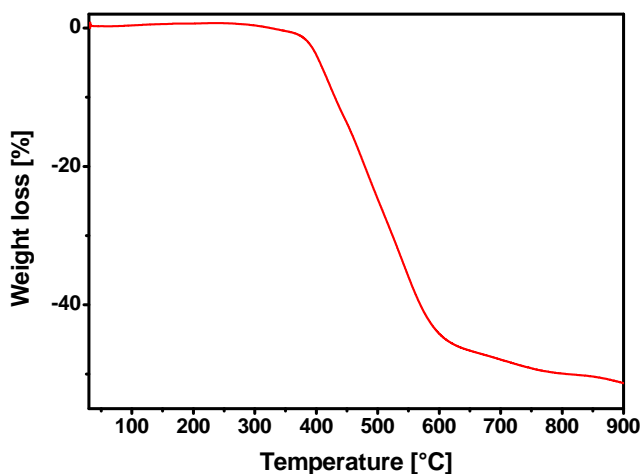


Figure 3: Thermogram of the electrocatalyst material under argon atmosphere.

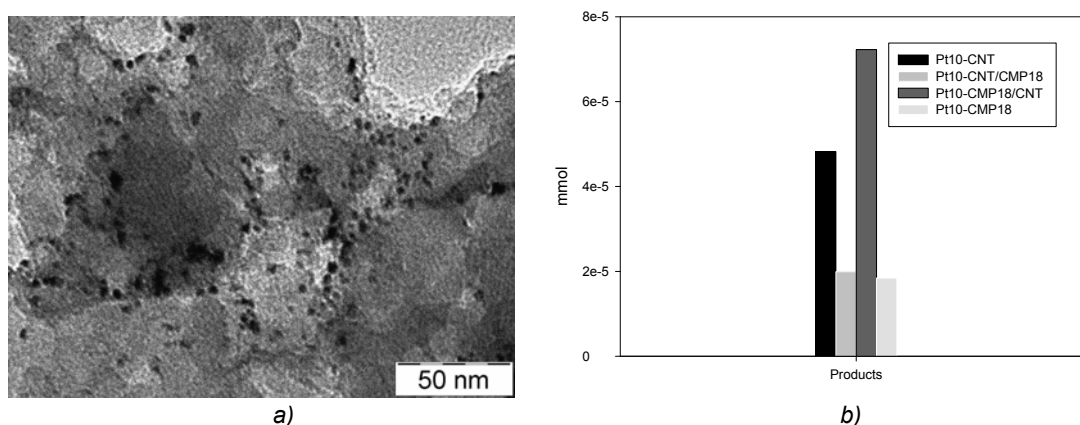


Figure 4: a) TEM image of Pt nanoparticles on the TPE-CMP surface; b) productivity for Pt doped CNT and TPE-CMP electrocatalysts (amount of metal: 10 wt. %, current: -20mA, $T=60^{\circ}\text{C}$).

The analysis by TEM showed that rather small Pt particles (about 5 nm dia.), well dispersed over TPE-CMP surface, are present and no abnormally large particles or many aggregates were observed (see Figure 4a).

4.2 Catalytic Test

Figure 4b shows the experimental results in terms of total hydrocarbon and oxygenate productivity for Pt/TPE-CMP electrocatalysts, compared with Pt deposited on CNT that is used as reference sample. The electrocatalytic reduction of CO_2 in solvent-less conditions is a very complicated reaction. The presence of microporous conjugated polymers can enhance the process performances due to their intrinsic porosity and high CO_2 absorption capability that increase the local concentration of CO_2 close to the catalytic sites (Pt nanoparticles). A proper assembly of the electrocatalytic layers is very important to guarantee a good proton mobility and a high electron conductivity. For this reason the doping of the CMP with active metal is not sufficient to increase the productivity compared to Pt on CNT probably due to a loss of conductivity. But, as shown in the figure, it was sufficient to add a little quantity (30 wt. %) of CNT to increase considerably the productivity (sample Pt10-CMP18/CNT). It is to notice that higher chain hydrocarbons (C3-C8) were detected in all the testing experiments (as well as hydrogen, carbon monoxide and methane were detected in the produced gas flow), but here we have limited our analysis to the liquid fractions C1-C3 (methanol, isopropanol, ethanol, acetic acid, acetaldehyde etc) which we was able to collect by a cold trap and identify unequivocally; we reported their production in the graph of Figure 4b as total amount (in mmol). In order to analyse the role of the Pt-nanoparticle localization, we also tried to mix Pt10-CNT with 30 wt. % of pure polymers (TPE-CMP). In this case, it can be observed that there is a worsening in the total productivity with respect to the reference sample, probably due to a dilution effect of the active phase. We may conclude that is of great importance the localization of the active phase (Pt), which should be deposited on the polymer surface where CO_2 absorption occurs.

The faradic efficiency was also very high for all the tests (>95 %) even if the major part refers to the side reaction of water splitting.

5. Conclusions

In this contribution we have investigated the behaviour of conjugated microporous polymers (TPE-CMP) doped with Pt nanoparticles as electrocatalysts in the process of CO_2 reduction back to liquid fuels. The experimental tests were performed in a novel electrochemical cell working in gas phase at 60°C by applying a small bias (-20 mA) between the working and counter electrodes. The advantages of operating in gas phase with respect to a slurry reactor were presented, particularly for what concerning the easier recovery of products. The correct design of the electrochemical cell is of paramount importance to increase the productivity and it is strictly related to the nature of the electrocatalytic materials used.

Results showed a relatively higher productivity by using the Pt-doped polymer as electrocatalyst, but it should be mixed to a small amount of CNTs to increase the electronic conductivity. Further experiments are in progress about the replacement of Pt with not-noble metal nanoparticles (such as Fe, Co). These

results are very promising and open new possibilities in the electrocatalytic conversion of CO₂ to liquid fuels by exploiting solar energy and closing the CO₂ cycle of its production/consumption.

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