

## Electrocatalytic Reduction of CO<sub>2</sub> for the Production of Fuels: a Comparison between Liquid and Gas Phase Conditions

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In this contribution we report on the electrocatalytic reduction of CO<sub>2</sub> for the production of liquid fuels by using two different approaches under i) liquid and ii) gas phase conditions. The main aim of the work is the comparison of these two experimental setups, in terms of productivity, kinds of liquid compounds produced and efficiencies, due to the differences in the mechanism which underlay the reactions occurring. Particularly, gas phase CO<sub>2</sub> reduction has some advantages such as ease in recovery of products, no CO<sub>2</sub> solubility issues and it allows the formation of oxygenates and hydrocarbons with higher chains (C<sub>2</sub>-C<sub>9</sub>). On the other hand, liquid phase CO<sub>2</sub> reduction yielded in higher productivity, giving formic acid and acetic acid as the major products and trace amounts of methanol. The experiments were performed in homemade electrochemical cells, designed on purpose to maximize the electrocatalytic area and reduce the volume of the cathodic hemi-cell. Initially, experiments were conducted using Cu thin film electrodes. Then, metal based nanostructured catalysts (using Fe and Cu, deposited on carbon-based substrates) were synthesized in order to improve the productivity and fine tune the selectivity in achieving longer chain hydrocarbon fuels. The final perspectives of this study regard the integration of this electrocatalytic device with a photo-anode to obtain a sort of artificial leaf, which collects energy in the same way as the nature does, by capturing directly CO<sub>2</sub> and converting it back to fuels.

### 1. Introduction

The increase in the greenhouse gas emissions and the depletion of fossil fuel reserves, together with the ever increasing energy needs, set forth the path towards the sustainable production of energy and chemicals (Kondratenko et al., 2013). In this context, the production of solar fuels via photo-electrocatalytic reduction of CO<sub>2</sub> is one of the most attractive routes for sustaining the future energy needs, reducing fossil fuel consumption and closing the CO<sub>2</sub> cycle (Ampelli et al., 2014a). The key to make this process feasible and greener is the capability to capture solar energy and generate the power necessary to activate the reaction of CO<sub>2</sub> reduction, moving from electrocatalysis to photo-electrocatalysis (Ampelli et al., 2012a).

The main challenges in achieving the aforementioned objectives are i) developing novel catalytic materials that are both selective and active in performing the reduction reaction, ii) performing CO<sub>2</sub> reduction at low potentials and iii) give out desirable end-products over a long period (Ampelli et al., 2015). Unfortunately, most of the existing catalysts are neither very selective nor active. Most of them reduce CO<sub>2</sub> to CO or alkyl formates or alkyl acids, which cannot readily be used as fuels such as hydrocarbons or alcohols. The drawback of low photoconversion efficiency and selectivity may be overcome through the design of highly active photo-electrocatalysts from the point of adsorption of reactants, charge separation and transport, light harvesting, and CO<sub>2</sub> activation (Tu et al., 2014). Moreover, a correct evaluation of the engineering aspects of the electrochemical device, in terms of reactor configuration, is needed to attain the maximum benefits from the electronic and irradiation pattern, as well as the proton conductivity for closing the electric circuit (Ampelli et al., 2009).

In this context, we developed both novel catalytic materials and setups to be used in the CO<sub>2</sub> reduction process trying to enhance the photo-conversion into liquid fuels. The general aim of this contribution is to compare two different approaches in performing the CO<sub>2</sub> reduction: i) liquid phase and ii) gas phase conditions. Particularly, in this paper we describe the novel design of a liquid phase electrocatalytic device, while we already described our homemade gas phase set-up elsewhere (Genovese et al., 2013a). The liquid phase electrochemical cell consists of an electrocathode composed of metal nanoparticles (NPs) supported on C-based substrates. The reduction of CO<sub>2</sub> occurs onto the metal NPs through a recombination between electrons and protons coming from the anode side, separate from the cathode compartment by a proton selective membrane, while electrons are transported through an external wire. Although performing CO<sub>2</sub> reduction the liquid phase has some drawbacks (such as CO<sub>2</sub> solubility issues, recovery of products, etc.) that might influence the cost-effectiveness of the overall process, it has the advantages of providing higher productivity and producing a small number of products. To the best of our knowledge, there are very few papers reporting gas phase operation for the electrocatalytic CO<sub>2</sub> reduction (Ampelli et al., 2011a). Furthermore, all the experimental apparatus operating in liquid phase make use of pure metallic layers as electrocatalysts (Kuhl et al., 2012), which are very different from the metal nanocomposite electrocatalysts that we have developed for gas phase experiments (Ampelli et al., 2014b). In this regard, one of the aims of this work is to verify if metal nanocomposite materials may also be used in liquid phase conditions. This understanding has been achieved by studying the experimental behaviour of carbon-based electrocatalysts loaded with non-noble metal NPs (Fe, Cu) in both gas and liquid phase cells, and comparing results with those obtained by using standard pure Cu layer. In all the experiments a bias between working and counter electrodes was applied to provide electrons needed for CO<sub>2</sub> reduction, simulating solar energy exploitation. Separately, we are studying the photoanode materials (Ampelli et al., 2009) and the photo-reactor (Ampelli et al., 2011b) to be coupled with the cathode hemi-cell.

Moreover, the mechanism of H<sub>2</sub> formation as side reaction in the electrocatalytic process was also investigated. This aspect has poorly been studied in literature but is of paramount importance to enhance the overall process efficiency (Ampelli et al., 2014c).

## 2. Experimental

### 2.1 Preparation of Cu layer

Copper foil (thickness 1.0 mm, Aldrich, 99.999% metals basis) was used to prepare a reference working electrode. Before the use, Cu foil was treated by mechanically polishing (P400 sandpaper) until no discoloration was visible and then by electro-polishing in phosphoric acid (85 % in H<sub>2</sub>O, Aldrich, 99.99 % metals basis) under potentiostat conditions at 2.1 V. A graphite foil was used as counter electrode, placed at a distance of 1.5 -2 cm from the working electrode. This treatment allowed to etch away the copper oxide layer, finally leaving a clean, polished Cu foil.

### 2.2 Preparation of metal-doped carbon layer

Carbon black (Vulcan XC-72) was used as starting material for the synthesis of the electrocatalysts. The nature of the functional groups on the carbon surface plays a key role in the catalytic activity of the electrocatalysts. Thus, carbon black was functionalized by direct oxidative treatment in concentrated HNO<sub>3</sub>, thereby introducing oxygen functionalities on the carbon surface. In detail, 1 g of carbon black was suspended in 50 mL HNO<sub>3</sub> (65 % Sigma Aldrich) and treated in reflux at 100 °C for 3 h, following by rinsing until neutral pH, filtering, and drying overnight. Different types of oxygen functionalities were introduced by this treatment. The total quantity and relative distribution can vary as a function of the annealing post-treatment in inert atmosphere.

Then, metal NPs (Fe and Cu) were deposited on carbon black by incipient wetness impregnation methodology using an ethanolic solution containing the proper metal precursor, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, respectively. After drying at 60 °C for 24 h, the samples were annealed for 2 h at 350 °C. The total amount of metal loaded onto the carbon black surface was 10 wt. %. This amount was used in order to have a good comparison to that of the metal loading used in the electrocatalysts for PEM fuel cells (usually 10-20 wt.%), which corresponds to a metal loading in the final catalyst of about 0.5 mg/cm<sup>2</sup>.

### 2.3 Assembly of electrode

A proper assembly of the electrode materials is a key factor for the working of the electrocatalytic cell which requires a good contact and adherence of the different layers, as well as to optimize mass transport and maintain a proper humidity of the membrane. In both gas and liquid phase configurations, the procedure of assembling was very similar: an ethanol suspension of functionalized carbon black impregnated with metal

NPs, was deposited on a commercial gas diffusion layer (SIGRACET GDL 25BC, supplied by SGL Group), based on carbon fibres. After keeping for drying overnight, the working electrode is ready to be tested in liquid phase experiments while, for gas phase testing, a Nafion membrane must be attached in direct contact with the active phase to form a sort of a GDM (Gas Diffusion Membrane) electrode, very similar to those used in PEM fuel cells. Details for gas phase electrode assembly and cell configuration were reported elsewhere (Genovese et al., 2013b). For the liquid phase tests, the Nafion membrane was not in direct contact with the electrocatalytic materials, but it was located about in the middle of the device, separating the two hemi-cells, as described below.

## 2.4 Liquid phase electrocatalytic cell

The liquid phase electrocatalytic testing of CO<sub>2</sub> conversion was carried out in a homemade Plexiglas lab-scale (size of about 3 cm in diameter for the electrode) continuous electrocatalytic reactor, operating at room temperature. This cell simulates the cathodic part of a full PEC (Photo-Electro Catalytic) cell.

Figure 1 reports a schematic draw of the experimental apparatus of the PEC hemi-cell used in these experiments. The liquid phase electrocatalytic cell has a three-electrode configuration, with a Pt wire (as counter-electrode) and a saturated Ag/AgCl electrode (as Reference electrode) immersed in the cathode bath. The anode side of the cell (i.e. the side of the cell in contact only with Nafion membrane and not with the electrocatalyst) is filled with an electrolyte solution (0.5 M solution of aqueous KHCO<sub>3</sub>) with main purpose of providing the protons needed for the reduction which diffuse through the proton selective membrane (Nafion) towards the electrocatalyst.

The cathodic side of the cell (the electrocatalyst side) operates in contact with a constant flow of the electrolyte solution (KHCO<sub>3</sub>), saturated with CO<sub>2</sub> gas (gas flow rate of 10 mL/min) in a separate small tank. This is achieved by pumping the electrolytic solution with CO<sub>2</sub> into the cathodic chamber using a peristaltic pump from the CO<sub>2</sub> tank. A potentiostat/galvanostat (Amel mod. 2049A) was used to supply a constant voltage difference of 1 V between the electrodes.

The liquid products were collected from the CO<sub>2</sub> tank at times 1 and 3 h respectively and analysed using a <sup>1</sup>H NMR spectroscopy (Varian NMR 500). H<sub>2</sub> production was detected by sampling from the head space of the small tank at regular intervals and analysing by gas chromatography.

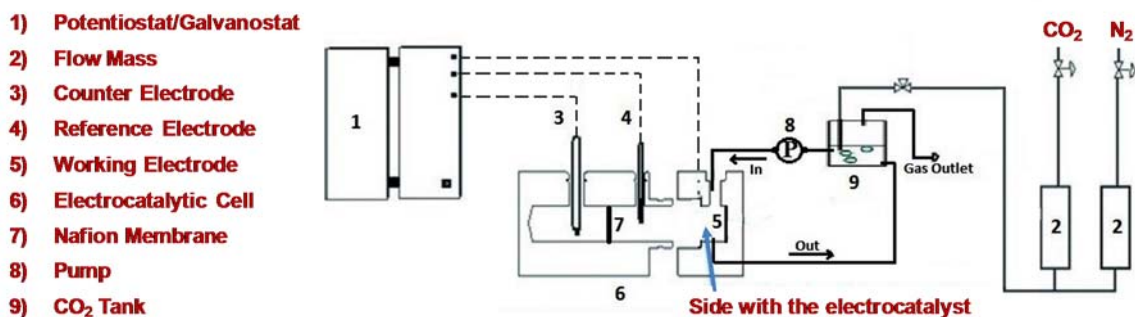


Figure 1: Schematic drawn of the experimental apparatus for Liquid Phase electrocatalytic tests of CO<sub>2</sub> reduction

## 3. Results and discussion

The electrochemical reduction of CO<sub>2</sub> involves multi-electron processes which can lead to a large variety of products ranging from CO to various oxygenates such as alcohols, aldehydes and carboxylic acids by a complex multistep mechanism that is probably quite different comparing gas and liquid phase conditions. The key aspect 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. Both gas and liquid phase devices were in fact designed taking into account these engineering aspects which are usually the critical factors limiting these kinds of cells. Particularly, the liquid phase electrocatalytic cell was designed on purpose to maximize the electrocatalytic area and reduce the volume of the aqueous solution. By applying a constant bias of 1 V between the electrodes, the current decreases (in absolute value) as a function of time-on stream during the first hour, stabilizing to a final value of about - 9 mA (see Figure 2).

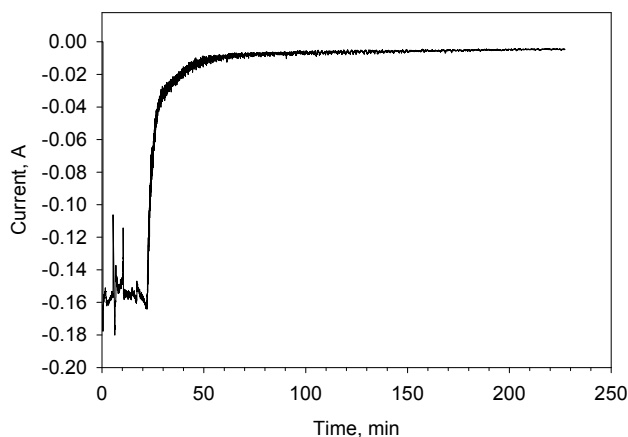


Figure 2: Current vs. time profile in liquid phase test for CO<sub>2</sub> reduction under potentiostatic mode (Cu NPs on carbon black, 1 V)

This behaviour is probably due to quenching phenomena of oxygen species, which adsorb on the Pt counter electrode surface increasing the overpotential of the cell. This phenomenon is similar to the overpotential for oxygen reduction usually found at a fuel cell cathode (Nørskov et al., 2004). Although tests were only performed by applying electric current to simulate solar energy, the irradiation of a highly photo-active material (Ampelli et al., 2008) may theoretically provide the current needed for CO<sub>2</sub> reduction, especially when aqueous organic wastes are processed (Ampelli et al., 2013).

For a comparison, Figure 3 shows the total productivity of liquid products in gas and liquid phase experimental tests in the process of CO<sub>2</sub> reduction.

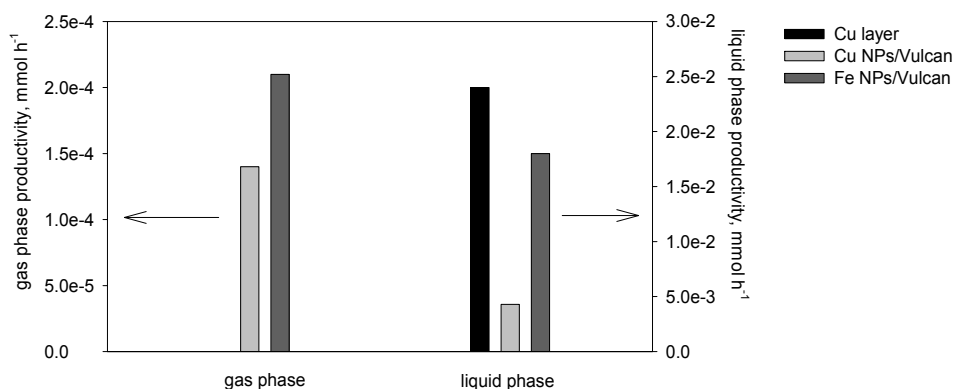


Figure 3: Total productivity in gas and liquid phase tests of CO<sub>2</sub> reduction

The first evidence is that the prepared metal NPs/Vulcan electrocatalysts work not only in gas phase (Genovese et al., 2013c), but also in our novel designed liquid phase electrocatalytic device. Liquid phase experiments showed a total productivity until two orders of magnitude higher than gas phase experiments depending on the electrocatalyst. Fe NPs/Vulcan evidenced higher productivity than Cu NPs/Vulcan both in gas and liquid phase tests. Cu layer gave the maximum of productivity, probably for its high conductivity with respect to Vulcan. On the contrary, the carbon support plays multiple roles: (i) allows the dispersion of the metal nanoparticles and especially (ii) determines the effectiveness of transport of electrons and protons to the metal nanoparticles for the electroreduction of CO<sub>2</sub>. We believe that the use of nanocarbons (carbon nanotubes or other advanced nanostructured carbons) instead of carbon black, may strongly improve

performances in liquid phase CO<sub>2</sub> reduction (Ampelli et al., 2014d). Synthesis of these metal-doped nanocarbon materials is under progress.

Operating in gas phase may have many benefits with respect to liquid phase: no problems of CO<sub>2</sub> solubility, easier and less costly recovery of the products. Moreover, the reaction mechanism of CO<sub>2</sub> reduction is probably quite different in gas phase and longer chains of products are obtained. Table 1 reports the different product distribution obtained in liquid and gas phases.

Table 1: Comparison of types of products obtained in liquid and gas phase in CO<sub>2</sub> electrocatalytic reduction

Gas phase	Liquid phase
Methanol	
Acetaldehyde	
Ethanol	Formic acid
Acetone	Acetic acid
Isopropanol	Methanol (in traces)
Hydrocarbons C4-C9 (in traces)	

Oxygenates and hydrocarbons were the main liquid products in gas phase tests, while liquid phase experiments mainly produced formic acid, acetic acid and traces of methanol. On the other hand, liquid phase electrochemical CO<sub>2</sub> reduction: i) yielded higher quantity of products, ii) gave formic acid as the main product, which may be used in formic acid fuel cells or as a vector to store and transport H<sub>2</sub>. Its reaction of synthesis is reversible, and formic acid can catalytically be decomposed under mild conditions to form back H<sub>2</sub> and CO<sub>2</sub> (Forenc, 2008). In liquid phase tests, the C-C bond formation to give acetic acid, increased in the later reaction times (after 3 h) as it is more difficult to form than formic acid. Methanol started to form (only in traces) after 3 h of reaction.

Another important aspect to take into account is the side reaction of water electrolysis, which unavoidably occurs in such kinds of devices, because unfortunately the standard reduction potential of H<sub>2</sub>O to form H<sub>2</sub> is considerably lower than the standard reduction potential of CO<sub>2</sub> to form CO<sub>2</sub><sup>-</sup> (Indrakanti et al., 2009). Table 2 reports the H<sub>2</sub> productivity obtained in gas and liquid phase experimental tests as side-product in the process of CO<sub>2</sub> reduction.

Table 2: H<sub>2</sub> productivity in gas and liquid phase experimental tests

electrocatalyst	H <sub>2</sub> productivity (mmol h <sup>-1</sup> )	
	gas phase	liquid phase
Cu NPs / Vulcan	1.2 e-1	2.3 e-3
Fe NPs / Vulcan	1.3 e-1	2.8 e-3

H<sub>2</sub> productivity is much lower in liquid phase with respect to gas phase, probably because overpotential phenomena are more consistent in liquid phase, diminishing the effective current between the electrodes. One of the possible routes to improve selectivity to liquid fuels and diminish side hydrogen production is to inhibit the surface reaction towards H<sub>2</sub> formation, i.e. by selectively blocking the surface sites with strongly chemisorbed species (for example, alkanethiols) or by modification of the electrocatalyst.

#### 4. Conclusions

In this contribution we presented a novel designed electrocatalytic device for CO<sub>2</sub> reduction to liquid fuels. The cell consists of two hemi-cells, separate by a proton selective membrane, with a three-electrode configuration operating in liquid phase. We described in detail the experimental apparatus, the preparation and assembly of the electrocatalyst, and reported results in terms of total productivity of liquid fuels. The electrocatalysts were based on carbon black deposited on carbon fiber layer, doping with metal (Fe, Cu) nanoparticles which act as catalytic sites for CO<sub>2</sub> reduction. All the electrochemical cells shown in literature use pure metal layers as electrocatalysts to reduce CO<sub>2</sub>, and operate in liquid phase. Recently, we demonstrated the possibility to perform the reaction also in gas phase, obtaining the production of high chain hydrocarbons and alcohols (until C9). Now, the aim of the present work has been to test these advanced metal-carbon based electrocatalysts also in liquid phase by using the present electrochemical device, designed on purpose to maximize the electrocatalytic area and reduce the volume of the aqueous solution. The mechanism of H<sub>2</sub> formation as side reaction in the electrocatalytic process was also investigated.

Results showed that liquid phase CO<sub>2</sub> reduction allowed to obtain higher productivity, giving formic acid and acetic acid as the major products and trace amounts of methanol, minimizing also H<sub>2</sub> productivity with respect gas phase tests.

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