



Gas phase electrocatalytic conversion of CO₂ to syn-fuels on Cu based catalysts-electrodes



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ABSTRACT

A novel electrocatalytic system based on a low temperature proton exchange membrane (Sterion) was developed for the gas phase electrocatalytic conversion of CO₂. This configuration allows the introduction of renewable energy in the chemical production chain via fuels production from direct CO₂ electro-reduction at atmospheric pressure and low temperatures (below 90 °C). For that purpose, three different Membrane Electrode Assemblies (MEAs) based on three different Cu based cathodic-catalysts were prepared and characterized: Cu-G/Sterion/IrO₂, Cu-AC/Sterion/IrO₂ and Cu-CNF/Sterion/IrO₂; graphite (G), activated carbon (AC) and carbon nanofibers (CNF). Thus, H₂O was fed and electrolyzed on the IrO₂ anode of the cell, thereby supplying H⁺ across the membrane to react with CO₂ in the cathodic-catalyst and leading to the production of a mixture of syn-fuels (syn-gas, methanol, methane...). Remarkably, the nature of the cathodic-catalyst carbon support had a strong influence on the electrocatalytic activity and selectivity of the system. Hence, the Cu-AC-based cathodic-catalyst showed the highest CO₂ electrocatalytic activity, due to the highest surface area of the AC support and the larger metal dispersion of the Cu particles leading to acetaldehyde and methanol as the main reaction products. Besides the lower conductivity of the AC support, the lowest energy consumption values for CO₂ conversion and methanol and acetaldehyde production was also achieved with the MEA based on Cu-AC cathodic catalyst due to its higher electrocatalytic activity.

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1. Introduction

The shift from a fossil fuel based economy towards a renewable energy one is a central strategy for achieving sustainability and energy efficiency in the chemical industry. In this regard, reducing CO₂ emissions is the key to proceed effectively in this direction. Two main technologies have been proposed so far: (i) capture and geological sequestration of CO₂ [1] and (ii) conversion into useful low-chain carbon fuels [2]. Sequestration still has certain barriers that make it unaffordable from an industrial point of view, such as the high cost of CO₂ capture, separation, purification and transportation. On the other hand, conversion into fuels seems to be a more attractive and promising solution that can meet the growing energy demands. The chemical conversion of CO₂ can be effectively performed via hydrogenation reactions [3–5]. This conversion can

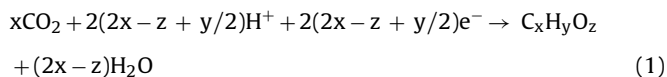
be achieved by chemical [6,7], photocatalytic [8], electrocatalytic [4,9–12], biological [13] and reforming [14] routes. Among them, the electrochemical pathway has been recognized as an efficient way to convert CO₂ to energy-rich products. The process possesses several advantages, namely: (i) control of the process by electrode potentials and reaction temperature; (ii) the supporting electrolytes can be fully recycled so that the overall chemical consumption can be minimized to simply water or wastewater; (iii) the electrochemical reaction systems are compact, modular, on-demand, and easy for scale-up applications; (iv) the electricity used to drive the process can be potentially obtained from a renewable source; (v) no external H₂ is required for the CO₂ reduction process as H⁺ are in situ generated within the process. Hence, the valorization of the CO₂ molecule by electrochemical reduction has attracted worldwide interest due to its potential environmental and economic benefits [2,15–17]. This technology, when coupled to a renewable energy source such as solar and wind, could generate carbon neutral fuels or high added-value chemicals that are conventionally derived from petroleum at a competitive price. As a

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matter of fact, the electrochemical reduction of CO₂ using a liquid electrolyte, either aqueous or organic, is being actively investigated in literature [18,19]. However, the main drawback of these processes is the recovery of the reaction product from the liquid electrolyte as the energy required to separate the products is higher than the energy stored in the produced molecules [10]. In this sense, the gas phase electrocatalytic conversion of CO₂ to liquid fuels allows easy product separation since there are no problems of solubility of CO₂ as in the case of liquid phase/electrolytes and no needs to recover the products from a liquid phase. Thus, gas-phase electroreduction of CO₂, mainly developed by the group of Prof. Centi [4,9–12], represents a valuable opportunity to incorporate renewable energy into the value chain of chemical industries. In this regard, the obtained products contain a higher energy density and are easier to transport and store. These previous studies have mainly used catalyst based on metal nanoparticles such as: Fe and Pt [4,9–12], Co [4] and Cu [4] supported over carbon nanotube (CNT) type materials. It has been shown that the nature of the nanocarbon substrate plays a relevant role in enhancing the productivity and tuning the selectivity towards c-chain products. However, the main disadvantage of this process is to control the localization of metal particles at the inner or outer surface of CNT which affects the obtained product distribution.

The gas phase electrocatalytic conversion of CO₂ is based on the use of a low temperature Proton Exchange Membrane (PEM) reactor configuration, consisting on a membrane electrode assembly (MEA) formed by an Anode/Membrane/Cathode system. Water is electrolyzed at the anode of the cell leading to the formation of O₂ and H⁺ which are electrochemically supplied across the membrane to the cathodic-catalyst where they react with the adsorbed CO₂, leading to the formation of different molecules according to the following general reaction:



Hence, the influence of the cathodic-catalyst may have strong importance on the resultant electrocatalytic activity of the system.

In contrast to previous studies [4,9–12], this work reports for the first time a systematic study based on three different Cu cathodic-catalysts prepared on three different carbon supports: graphite (G), activated carbon (AC) and carbon nanofibers (CNF). The use of carbon materials has proven to be the best catalyst supports for such applications due to their specific properties, such as acid and base resistance, porosity, conductivity and the possibility of recovering the metals by combustion of the supports [20]. As a result, carbon materials have been used as conductive substrates for metal nanoparticles in electrocatalysis for the conversion of CO₂ [4,10,11]. The use of carbon-based electrocatalysts, e.g. similar to those used in PEM fuel cells, is critical to obtain good performances and control the selectivity in CO₂ conversion. In this sense, carbon support plays multiples roles in these types of systems by allowing a good dispersion of metal nanoparticles and especially facilitates the effectiveness of electrons and protons transport due to a better distribution of the metal nanoparticles [4]. On the other hand, copper was selected as catalyst due to its lower cost vs. other typically used materials. Additionally, a previous work [4] based on copper catalyst supported on carbon nanotubes showed its better performance among other materials for the electrocatalytic conversion of CO₂ to alcohols production under solventless conditions." Hence, in this work the role of different carbon supports as well as the influence of the applied current and reaction temperature on the catalytic activity and selectivity of the gas phase electrocatalytic conversion of CO₂ have been studied.

2. Experimental

2.1. Preparation of the Cu carbon supported cathodic catalysts

Copper catalysts supported on G, AC and functionalized CNF were used as cathode materials of the electrocatalytic reactor. Iridium (IV) oxide (IrO₂) was used as the anode.

Commercial graphite (Aldrich), commercial active carbon (Panreac) and synthesized functionalized carbon nanofibers were used as starting materials. Carbon nanofibers were prepared by the catalytic chemical vapor deposition method (CVD) in a fixed-bed reactor at atmospheric pressure. The synthesis was conducted over a Ni/SiO₂ (10%, w/w) catalyst at 600 °C to obtain fishbone type carbon nanofibers, employing ethylene as the carbon source and hydrogen as the carrier gas (C₂H₄/H₂, 4/1, v/v, 900 Ncm³ min⁻¹). The carbon deposit obtained was demineralized using HF (48%, v/v) in order to remove the parent catalyst particles and to avoid any residual Ni effect in later catalysts preparation/characterization steps. The material was dried for 12 h at 383 K in air to remove water prior to characterization. Further details regarding the CNF synthesis are given in a previous work [21]. The functionalization of the CNFs was performed by an oxidative treatment in HNO₃ to introduce oxygen functionalities on the carbon surface. Metal nanoparticles were later deposited on the graphite, active carbon and functionalized carbon nanofibers by the impregnation method. The different supports (G, AC and CNF) were placed in a glass vessel and kept under vacuum at room temperature for 2 h to remove water and other compounds adsorbed on the structure. A known volume of ethanolic solution of Cu(NO₃)₂·3H₂O (Panreac) (the minimum amount required to wet the solid) was then poured over the sample. After 2 h, the solvent was removed by evaporation under vacuum at 90 °C in a rotary evaporator. The catalysts were dried at 120 °C overnight, calcined in N₂ atmosphere at 350 °C using a heating ramp of 5 °C/min and kept at that temperature for 2 h. Finally, they were reduced in H₂ at 350 °C for 2 h (heating rate 5 °C min⁻¹). The total load of metal was around 50 wt.%.

2.2. Preparation of the electrodes and membrane electrode assembly (MEA)

The catalyst inks for the preparation of each electrode, anode and cathode respectively, were prepared by mixing appropriate amounts of the catalysts, IrO₂ commercial catalysts powders (Alfa Aesar, 99%), Cu-graphite powder, Cu-activated-carbon powder and Cu-carbon nanofibers powder with a Nafion solution (5 wt.%, Aldrich chemistry, Nafion® 117 solution) and isopropanol (Sigma Aldrich) with a binder/solvent volume ratio of 0.04. The selection of IrO₂ as the anode for the three explored MEAs has been done according to its unique and superior ability for water oxidation reaction in conventional PEM electrolyzers [22]. Then, the different inks were deposited on Carbon paper (Fuel Cell Earth) substrates at 65 °C until a metal loading of 0.5 mg cm⁻² for each electrode was obtained after drying. The geometric surface area of both electrodes was 12.56 cm² (4 cm of circular diameter electrode). A proton conducting Sterion® membrane of 185 μm thickness (supplied by Hydrogen works) was used as the electrolyte (H⁺ conductor material). Prior to use, the Sterion® membrane was treated by successive immersion at 100 °C for 2 h in H₂O₂ in order to remove organic impurities, in H₂SO₄ for activation and in deionized water to remove traces of solutions. Finally, in order to prepare the membrane electrode assembly (MEA), the membrane was sandwiched between the electrodes. Then, the whole system was hot-pressed using a press (GRASEBY SPEAC) at 120 °C and a pressure of 1 metric ton for 3 min.

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