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Treball Final de Grau

Ink optimization for the fabrication of Cu_2O -CeO₂ gas diffusion electrodes.

Optimització de la tinta per la fabricación d'elèctrodes de difusió de gas de Cu_2O - CeO_2 .

Júlia Orcera Busquets Gener 2024





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To the stars who listen and the dreams that are answered.

En primer lloc, vull agrair tota l'ajuda rebuda per part de l'Andreina i la Teresa durant el transcurs del treball.

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IDENTIFICATION AND REFLECTION ON THE SUSTAINABLE DEVELOPMENT GOALS (SDG)

This project was involved in two of the 5P's. These five "P" were: People, Prosperity, Planet, Peace, and Partnership. The 2P involved in it were Prosperity and Planet. This work helps in taking care of the planet (UN 13) and provides prosperity (UN 7 and UN 9) because uses new methods that makes the planet more prosper when they reduce carbon dioxide (CO₂) emissions.

The three sustainable development goals (SDG) compatibles with the 2030 Sustainable Development Agenda that conforms the 2P are:



- UN number 7 (affordable and clean energy) because the method decarbonizes the energy sector by reducing carbon dioxide emissions through CO₂ electroreduction.
- UN number 9 (Industry, innovation, and infrastructure) due to the technology used in this work is an electrochemical reactor configured by a gas diffusion electrode, which can convert CO₂ into chemical products. This technology can be scaled up and operated for a long time under environmental conditions.
- UN number 13 (Climate action) because we try to reduce carbon dioxide emissions by doing electroreduction of CO₂ coming from the industry and obtaining other products like ethylene, methane that have more uses in the industry.

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1. SUMMARY

 CO_2 emissions are a very famous problematic nowadays because it is what causes the greenhouse effect and the climate change. One way for reducing these emissions is doing an electrochemical reaction and convert CO_2 into other products like: ethylene (C_2H_4), methane (CH_4), methanol (CH_3OH), carbon monoxide (CO), et al. In this project, this problematic was treated, and we studied the CO_2 conversion into ethylene, because it is the product that has more uses in the plastic industry, it is a polymer and it can synthetize polyethylene, also it is the best product because does not contribute into the greenhouse effect how it can do methane or carbon monoxide.

At industrial level, ethyne production can be performed on an electrochemical flow cell, whose design requires the implementation of a gas diffusion electrode (GDE). Under this configuration, the electrochemical reaction will take place when the CO₂ flow is activated on the electrode. The GDEs are usually composed by a support (carbon paper), a microporous layer, and a catalyst layer (cooper-based catalyst). For the catalyst layer deposition, a stable ink formulation (solvent+ ionomer + catalyst + PTFE) is required to guarantee a hydrophobic catalyst layer.

In this context, the main goal of this work is to optimize the ink composition for the fabrication of an active Cu₂O-5 wt.%CeO₂ GDE of 5 cm². With this aim, the catalytic material was first scaled-up. Then, the stability of the ink composition was studied using different catalyst/solvent and nafion/solvent ratios. Sequentially, the stability of the ink was also evaluated using different solvents (ethanol, water, isopropanol). Finally, for the most promising ink formulation, the addition of 5wt% of polytetrafluoroethylene (PTFE) was evaluated in order to improve the hydrophobicity properties of the electrodes. In all prepared GDEs, catalyst characterization and CO₂ electrochemical evaluation were performed to select the optimum GDE able to produce efficient C_2H_4 .

The results of stability suggested that the ink formulation composed by isopropanol as solvent (10 mL), nation as ionomer (280 μ L) and Cu₂O-5 wt.%CeO₂ (40 mg) as catalyst is the most promising for scale-up GDE of 5 cm². In this electrode, the faradaic efficiency (FE) to ethylene

achieved was close to 56%. Furthermore, the addition of PTFE was found to be positive since a more hydrophobic GDE was fabricated, and thus an improved FE to ethylene was achieved (60%). The high GDE performance was attributed to the use of the solvent. Isopropanol appears to create rougher surfaces, smaller cubic particles, and a thin catalyst layer.

Keywords: CO₂ electroreduction, Cu₂O-CeO₂ catalyst, gas diffusion electrodes, ink optimization, Ethanol, isopropanol, carbon paper, PTFE, flow cell.

2. RESUM

Les emissions de CO₂ són una problemàtica actual, ja que són els causants de l'efecte hivernacle i destrossen la capa d'ozó provocant el canvi climàtic. Una manera per reduir aquestes emissions de carboni és fer una reacció electroquímica i convertir el CO₂ en altres productes com poden ser l'etilè (C₂H₄), metà (CH₄), metanol (CH₃OH), monòxid de carboni (CO), etc. En aquest treball es tracta aquesta problemàtica i el producte principal que volem obtenir és l'etilè, ja que aquest és un polímer molt utilitzat en la indústria, i a partir del qual es pot obtenir el polietilè. I a més és un producte que no provoca efecte hivernacle com es el cas del metà.

En l'àmbit industrial es pot produir etilè fent ús d'una cel·la de corrent continu que contindrà un elèctrode de difusió de gas (GDE de les seves sigles en anglès) i en el qual es farà passar un flux de corrent i un flux de CO₂ que reaccionarà per donar els productes esmentats. L'elèctrode de difusió de gas està format per un suport fet de paper de carboni microporós, una capa microporosa i la capa del catalitzador, en aquest cas un catalitzador de base de coure. Per fer la capa del catalitzador es necessita una tinta (solvent+ ionòmer+ catalitzador+ PTFE) que sigui estable i que garanteixi la hidrofobicitat d'aquesta capa.

El que es farà en aquest projecte, per tant, és escalar la tinta per fer fabricar elèctrodes de Cu₂O-5 wt.%CeO₂ de dimensió 5 cm². Per aconseguir-ho, en primer lloc, s'ha d'escalar la reacció de producció de catalitzador, en segon lloc, s'estudiarà l'estabilitat de la tinta buscant quines són les millors relacions catalitzador/solvent i Nafion/solvent per treballar, en tercer lloc, s'estudiarà l'estabilitat usant tres solvents diferents: l'etanol, l'aigua i l'isopropanol, i per acabar, s'estudiarà la incorporació del 5% en pes de politetrafluoroetilè (PTFE) a la millor tinta. El PTFE s'afegeix per augmentar la hidrofobicitat de l'elèctrode. Un cop preparats aquests elèctrodes es farà la seva caracterització (angle de contacte i microscopi electrònic de rastreig), i s'avaluarà el seu rendiment per la producció d'etilè (C₂H₄) en la reacció electroquímica del CO₂.

Els resultats obtinguts a les proves d'estabilitat conclouen en què la millor tinta per preparar els elèctrodes de 5 cm² està formada pels següents: solvent, ionòmer i catalitzador que són isopropanol (10 mL), Nafion (280 µL) i Cu₂O-5 wt.%CeO₂ (40 mg) respectivament. Per la tinta

preparada amb isopropanol i isopropanol amb PTFE les eficiències faradaiques per l'etilè son 56% i 60% respectivament. L'addició del PTFE es considera exitosa, ja que fa augmentar l'eficiència faradaica. L'alt rendiment per l'obtenció de l'etilè s'ha relacionat a l'efecte de l'isopropanol, pel fet que aquest solvent fa que la capa del catalitzador sigui més rugosa, a més les partícules cúbiques són més petites, i la capa del catalitzador és més fina.

Paraules clau: electroreducció de CO₂, cel·la electroquímica, catalitzador de Cu₂O-CeO₂, elèctrode de difusió de gas, optimització de la tinta, etanol, isopropanol, paper de carboni, PTFE.

3. INTRODUCTION

Carbon dioxide emissions continue to be a critical concern globally because of their significant impact on climate change. These emissions primarily result from human activities such as burning fossil fuels for energy, industrial processes, deforestation, and transportation.

The consistent rise in CO₂ levels contributes to the greenhouse effect, trapping heat in the Earth's atmosphere and leading to rising temperatures, extreme weather patterns, sea level rise, and other detrimental effects on ecosystems and human societies[1].

In 2023 (see Figure 1[2]), approximately 36.8 billion tons of carbon dioxide were released to the atmosphere, that is 3.6 times than 8 years ago. Addressing and reducing CO₂ emissions remain imperative to mitigate the adverse impacts of climate change and safeguard the planet for future generations.



Figure 1: Annual carbon dioxide (CO_2) emissions worldwide from 1940 to 2023 (in billion metric tons). Source: Statista 2023.

The electroreduction of CO₂ (CO₂RR) has emerged as a promising technology in the quest to mitigate CO₂ emissions[3]. As shown in Figure 2, this process involves the use of electrical energy to convert carbon dioxide into valuable products such as carbon monoxide, methane, methanol, formic acid, or ethylene. By harnessing renewable energy sources like solar or wind power, this electrochemical conversion method offers a sustainable pathway to transform CO₂ into useful chemicals, thereby reducing its environmental impact.



Figure 2: A schematic representation of the electroreduction of CO₂

In the context of CO₂RR, electrochemical reactors must be used to facilitate the electrochemical conversion of carbon dioxide into valuable products. A flow cell is typically used as the electrochemical reactor for industrial applications. Its design allows for the continuous flow of CO₂ and electrolyte through the electrochemical cell where the reduction reactions take place.

In a flow cell for CO₂RR, the configuration typically includes:

- Electrodes: These electrodes are often made of specific materials or catalysts designed to promote the reduction of carbon dioxide into desired products.
- Electrolyte: The electrolyte solution facilitates the transfer of ions between the electrodes and supports the electrochemical reactions. It helps to maintain conductivity and provides the necessary medium for the reduction of CO₂.
- **Continuous flow:** The flow cell allows for a constant flow of CO₂-enriched electrolyte through the cell, ensuring a steady supply of reactants to the electrodes.

This configuration is crucial for studying CO₂ electroreduction under controlled conditions and assessing the efficiency, selectivity, and scalability of the electrochemical process. Flow cells in CO₂RR research allow for better control over reaction conditions and enable the exploration of

various electrode materials and operating parameters to optimize the conversion of CO₂ into valuable chemicals or fuels.

3.1. CO₂RR to Ethylene

Ethylene[4] (C_2H_4) is the most important organic compound used in industry because it can be used as a feedstock in the production of polymers like polyethylene, used for manufacturing fibers, bottles, food packaging. In particular, polyethylene (CH_2 — CH_2)_n is the simplest type of polymer. It has a lot of applications and is simple to fabricate and is less expensive than other polymers. Other applications include industrial chemicals, such as ethylene oxide, ethylene glycol, polyglycols and different types of ethanolamine. Therefore, by converting CO_2 into ethylene through electrochemical processes powered by renewable energy sources, this technology offers the dual advantage of reducing greenhouse gas emissions while simultaneously providing a pathway to produce a crucial industrial feedstock.



Figure 3: Mechanism of CO₂RR [16]

The different mechanism reactions for CO₂ electroreduction can be seen in Figure 3. From this reaction pathway ethylene, methane, ethanol, methanol, formic acid, or carbon monoxide can be obtained.

3.2. Catalyst for ethylene production

Copper, as a metal (Cu⁰) or as a metal oxide (CuO and Cu₂O), is typically used as the catalyst in the CO₂RR for the production of C₂H₄ [5]. This is because copper is a relatively abundant and cost-effective metal compared to other precious metals, making it more accessible and feasible for large-scale applications. Additionally, copper surface can exhibit multiple oxidation states, granting its versatility as a catalyst in the electrochemical conversion of CO₂. This variability in copper's oxidation states allows for the formation of various products, such as ethylene, by manipulating the surface structure and composition of the catalyst.

Recently, copper-based catalysts supported on and/or promoted by metal oxides (such as Al_2O_3 , ZrO_2 , La_2O_3 , CeO_2 , Al [6]) have been investigated to enhance the performance of the CO_2RR to C_2H_4 [7][8]. Among metal oxides, ceria (CeO₂) has proven to be a promising option since it facilitates the adsorption and activation of CO_2 on the surface of the copper catalyst, which promotes the selective formation of ethylene over other products [9].

3.3. Gas diffusion electrodes

Gas diffusion electrodes (GDEs) are specialized electrodes used in electrochemical flow cells, particularly in reactions involving gases like the electroreduction of carbon dioxide or the electroreduction of oxygen for obtaining hydrogen peroxide for environmental remediation like decontaminate water [10]. The electrodes are designed to facilitate the efficient interaction between gas molecules, such as CO₂, and the electrode surface where electrochemical reactions occur.

The electroreduction of CO_2 is a reduction-oxidation (redox) reaction. This means that CO_2 is reduced in the cathode forming ethylene, and water is oxidized into oxygen in the anode. The reaction medium used for the electrochemical reactions is alkaline how it shows the reactions below.

Cathode (reduction): $2 CO_2(g) + 8 H_2O(aq) + 12 e^- \rightarrow C_2H_4(g) + 12 OH^-(aq)$ Anode (oxidation): $4 OH^-(aq) \rightarrow O_2(g) + 2 H_2O(aq) + 4e^-$ Key components of gas diffusion electrodes typically include (See Figure 4 [11]):

- Porous substrate: Often made of materials like carbon or carbonaceous fiber structures (CFS), providing a high surface area for gas interaction and ensuring uniform distribution of gases over the electrode.
- Hydrophobic micro porous layer: This micro porous layer (MPL) prevents the accumulation of liquid on the electrode's surface, allowing continuous gas flow and maximizing the efficiency of gas diffusion to the catalyst.
- **Catalyst:** A catalyst layer (CL), frequently composed of metals is deposited onto the substrate. This catalyst promotes the desired electrochemical reactions.



Figure 4: Gas diffusion electrode

The hydrophobicity of the microporous layer is important for maintaining the gas diffusion layer impermeable preventing the adsorption of water on the layer. This is important because after some hours of operation under CO_2 electrolysis conditions it may occur electrolyte flooding in the GDE, if the electrolyte enters through the catalyst layer it makes the electrode unusable and it may block the gas flow through the cell by the appearance of water and carbonate salts [12].

The alkaline environment in contact with the catalyst layer during the electrolysis reaction favors ethylene selectivity by inhibiting the hydrogen reaction (HER) [13]. However, during the reaction the electrolyte precipitates in form of a carbonate salt that affects negatively to the hydrophobicity of the gas diffusion layer destabilizing the CO₂-catalyst-electrolyte interface used during the reaction.

One way to improve the hydrophobicity is to add polytetrafluoroethylene (PTFE) directly on the ink before this being sprayed on the carbon paper. Then, it will be studied if the addition of

PTFE also improves the faradaic efficiency to produce ethylene during the reaction or if it changes the selectivity of the product, or it does not affect in anything than the hydrophobicity.

The catalyst Cu₂O-5wt.%CeO₂ mentioned in section 3.2 has been tested before for the research group in 1x1 cm electrodes (1cm² surface) with 1mg/cm² of ink[14]. Then these gas diffusion electrodes were studied doing chronopotentiometry in an H-cell.

In this work the electrodes used have 5 cm² of surface (2.25 x 2.25 cm) how it is a bigger electrode the ink must be optimized, and the preparation of the catalyst must be scaled for obtaining more quantity in every synthesis. One more change that will be done is we will use a flow cell instead that the H-cell used previously. The principal difference between these two cells is that in flow cells the catholyte (and also the GDE) is directly in contact with the CO₂ flow.

4. OBJECTIVES

The main objective is to optimize the ink composition for the fabrication of an active Cu_2O-5 wt.%CeO₂ GDE of 5 cm².

For achieving this goal some specific steps had to be studied before:

- Scaling-up of the synthesis of the catalysts based on Cu₂O and promoted with 5 wt.% CeO₂.
- Study the stability of the ink composition (catalyst + ionomer + solvent) using different catalyst/ionomer/solvent ratio.
- Study the stability of the ink formulation by using different solvents (ethanol, isopropanol, water, and a mixture between them) at the most promising catalyst/ionomer/solvent ratio.
- Catalyst characterization and CO₂ electrochemical evaluation of the prepared GDEs to select the most promising to produce C₂H₄.
- Study of the effect of the addition of PTFE in the most promising ink compositions.

5. EXPERIMENTAL SECTION

5.1. REAGENTS AND INSTRUMENTS

5.1.1. Reagents

The chemical reagents and materials used for this project are shown in Table 1.

Chemical name	Chemical formula	Manufacturer	Quality
Cerium (III) nitrate hexahydrate	Ce(NO ₃) ₃ ·6H ₂ O	Sigma-Aldrich	99% trace metals basis
Copper (II) sulfate pentahydrate	CuSO ₄ ·5H ₂ O	Sigma- Aldrich (Supelco)	98%
L-ascorbic acid	HO OH OH OH	Sigma-Aldrich	99%
Sodium hydroxide	NaOH	Sigma-Aldrich (Supelco)	97%
Nafion (sulfonated tetrafluoroethylene)	$\begin{bmatrix} & F_2 & F_2 \\ F_2 & F_2 \\ & & F_2 \end{bmatrix}_{Y}$	Alfa Aesar	_
Polytetrafluoroethylene (PTFE)	F F F	QUINTECH	_
Ethanol absolute	CH ₃ CH ₂ OH	PanReac AppliChem	99.8%
Isopropanol	ОН	ACS Reagent	p.a. (>99.8%)

Table 1: Information of the reagents and materials

Milli-Q water	—	Synergy ©	—
Potassium hydroxide	КОН	ENSURE ®	85%
Proton exchange membrane Nafion® 117	$\begin{bmatrix} & & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ $	Alfa Aesar	_
Reference electrode	Ag/AgCl	Innovative instruments	—
Carbon dioxide	CO ₂	Linde	99.99%
Gas calibration bottle	95% He, 1% H ₂ , 1% CH ₄ , 1% CO, 1% C ₂ H ₄ , 1% C ₂ H ₆	Linde	99.99%
Stainless-steel paper		Bekaert	—
Nitrogen	N ₂	Linde	99.99%
Carbon paper with microporous layer	_	Freudenberg H23C6	—

5.1.2. Instrumental

The instruments and the software used in this work:

- Centrifuge Sorvall ST16. Thermo scientific
- Balance Mettler Toledo Classic PB303-S
- Termolab. Electric Oven
- Airbrush elite E4182

- Scanning electron microscope JEOL J-7100. AZtec© for energy-dispersive X-ray spectroscopy (EDS) analysis

- Logitech Glass lens RightLight 2 Technology.
- Contact angle software
- Shenchen Pump LabF1. Model YZ1515x
- Agilent 990 micro gas chromatograph.
- Potentiostat Princeton Applied Research VMP2, controlled by EC-Lab software

- Flow cell

- Bronkhost Mass Flow Controllers, with FlowDDE software for controlling gas flows.

5.2. PREPARATION OF THE CATALYST

5.2.1. Preparation of Cerium (VI) Oxide

CeO₂ nanoparticles were synthesized by hydrothermal method. First, a solution of 7 mL of 0.5M Ce(NO₃)₃·6H₂O was prepared. Sequentially, a solution of 50 mL of 4.5M NaOH, and the first solution was added dropwise into the NaOH solution, the mixture was stirred for 30 minutes. After this time, the crystal growth was performed in an autoclave reactor at 240 °C for 24 hours.

Then, the cerium oxide powder was washed three times using milli-Q water and separated by centrifugation for 10 minutes (10000 rpm each time).

5.2.2 Synthesis of Cu₂O-5wt.%CeO₂

For a 1g-batch, 50 mL of 0.02M CuSO₄·5H₂O [15] and 0.012g of CeO₂ (5% of the weight of CuSO₄) were dissolved in milli-Q water and ultrasonicated for 30 minutes. Then, 50 mL of 0.4M NaOH were added by dropwise into the solution and 0.707 g of L-ascorbic acid, finally was added and stirred for 30 more minutes. The Cu₂O-5wt.%CeO₂ was centrifugated for 10 minutes at 10000 rpm and then washed three times with absolute ethanol. The catalyst was dried overnight at 80°C.

For a 5g-batch, two scaling synthesis procedure were considered for the catalyst preparation. The first method used was similar to the previous synthesis, but the quantities were scaled 5 times more than the initial one, that was 250 mL of CuSO₄·H₂O 0,02M; 0,126g CeO₂; 250 mL NaOH 0,4M; 3,536 g L-ascorbic acid. The second method was simply joining the products of five 1g-batches. As CeO₂ agglomeration was detected in SEM-EDS analysis, an extra stirring time of 30 min was used after sonification to homogenize the solution.

5.3. GAS DIFFUSION ELECTRODE FABRICATION

5.3.1. Ink preparation

The ink formulation (it is called ink because this solution that forms this layer when sprayed must be dried) used as starting point for the manufacture of the gas diffusion electrode was composed by three components:

- The catalyst (20 mg of Cu₂O-5wt.%CeO₂)
- An ionomer (140 µL of Nafion©)
- The solvent (0.5 mL of Ethanol)

This ink composition was considered according to previous work performed by the group for an electrode of 1 cm². As part of the ink preparation, the mixture of the components was sonicated for 30 minutes. Then, the ink was airbrushed covering all the area of the support. In this study, carbon paper was used as the support. Prior to the catalyst deposition, the carbon paper was fixed on a metallic holder and heated up to a temperature of 60°C to guarantee the evaporation of the solvent. The correct amount of catalyst mass on the carbon paper support was fixed to 1 mg/cm².



Figure 5: Shows the process of spraying GDE. a) support and carbon paper, b) airbrush pistol

5.3.2. Study of the stability of the ink composition

As the goal is to optimize the ink composition, a first set of experiments were carried out to study the stability of the ink (catalyst + ionomer + solvent). For these experiments, the amount of catalyst (20 mg) and ionomer (140 μ L) was kept constant, while the amount of the solvent (ethanol) was varying from 500 to 5000 μ L.

Once the inks were prepared, they were sonicated for 30 minutes. Then, all the inks were located on a smooth surface and kept in a static position for the evaluation of their stabilities. The precipitation of the nanoparticles was registered by a photo at different times (0h, 1h, 2h, 3h, 4h, 5h and 24h).

5.3.3. Study of the ink formulation using different solvents

In order to evaluate the effects of the solvents in the stability of the ink formulation, a new set of experiments were performed at the most promising ink composition (section 5.3.1).

For these experiments, it is important to say that the amount of the most promising ink composition was also scaled-up to achieve enough ink for the fabrication of the gas diffusion electrode of 5 cm². Therefore, the ink formulation was composed by 40 mg of catalyst, 280 μ L of ionomer and 10 mL of solvent. The solvents evaluated were ethanol, water, isopropanol, and combination between them. As in the previous study, photos were recollected at different times: 0h, 1h, 2h, 3h, 4h, 5h and 24h.

After the stability study, all the inks were sprayed on a carbon paper (2.25 cm x 2.25 cm). The amount of catalyst mass was fixed to 1 g/cm².

5.3.4. Study of the effect of PTFE in the ink

Finally, the study of the effect of the addition of PTFE (5 wt.%) was carried out at the most promising ink formulation (section 5.3.2.). In Table 4 (section 7.3) is shown the ink formulations with and without the addition of PTFE. Once all the inks were prepared, they were sonicated for 1 hour. Then, all the inks were located on a smooth surface and kept in a static position for the evaluation of their stabilities. The stability of the ink was also analyzed at different times (0h, 1h, 2h, 3h, 4h, 5h and 24h).

After the study of stability, the inks are sprayed on a carbon paper, keeping 1 mg/cm² of catalyst mass. For the activation of the PTFE, the electrodes were treated under a N₂ atmosphere on an oven for 2h at 250°C. The temperature ramp used was 2° C/min.

5.4. GAS DIFFUSION ELECTRODE CHARACTERIZATION

5.4.1. Catalyst

The surface morphology and elemental composition was investigated using a JEOL J-7100 high-resolution SEM equipped with an EDS detector (Oxford instruments) and AZtecEnergy software. Prior to EDS analysis, catalysts were fixed over an aluminum holder with a carbon tape. The elemental analysis was carried out at 20 kV and restricted to Cu, Ce, and O to avoid inconsistent results.

5.4.2 Gas diffusion electrode

The transversal section of the catalyst layer for each electrode was also investigated using a JEOL J-7100 high-resolution SEM using an inclination angle of 40°. For the thickness estimation of the transversal section, we use Eq. 1.

$$y = x \cdot \cos(\alpha) \tag{1}$$

Where «y» is the real thickness of the transversal section, «x» the thickness observed, and « α » the angle of the sample. In this case is 40°.

Furthermore, the surface of the electrodes was studied at different magnification (x50, x300, x10,000 and x43,000).

Finally, the surface-wetting was investigated using contact angle measurements. For the experiments, a drop of 20 μ L of Milli-Q water was used. The contact-angles images we recorded using a Logitech Glass lens RightLight 2 Technology.

5.5 ELECTROCHEMICAL REDUCTION OF CO_2 to C_2H_4



Figure 6: Set-up of the cell for doing CO₂ electroreduction. Left, anode. Right, cathode side.

The performance evaluation of the CO_2RR to C_2H_4 of the gas diffusion electrodes were performed on an electrochemical flow cell. As can be seen in Figure 6, the flow cell design was composed by an anode and cathode section.

In the cathode section, the CO_2 and catholyte were flowed through their respective chambers. A CO_2 flow rate of 200 mL/min was used and controlled by a mass flow controller (MFC, Bronkhorst). The working gas diffusion electrode had a projected area of 5 cm², while a stainlesssteel paper of 9 cm² was used as the counter electrode, located at the anode section.

The catholyte chamber is separated from anolyte chamber by a proton exchange membrane (PEM, Nafion® 117). The total volume of the electrolyte used was 200 mL. In both cathode and anode chambers, the aqueous electrolyte (1 M KOH) rate was set at 20 mL/min and supplied with a peristaltic pump.

The pump used was calibrated (See appendix 2.1) for adjusting the flow when doing the experiments, and it was done by measuring the flow during a certain time and then plot flow vs time for obtaining the calibration equation.

The reference electrode was an Ag/AgCl electrode. The potential values were then transformed into RHE (Reversible Hydrogen Electrode) voltages by using Eq. (2).

$$E(vs. RHE) = E\left(vs. \frac{Ag}{Agcl}\right) + 0.222V + 0.059V * pH$$
 (2)

For each electrode, the faradaic efficiency (FE) was evaluated by varying the current density from -250 to -1500 mA/cm² (Δj = -250 mA/cm²) and using chronopotentiometry (Potentiostat-Princeton Applied Research VMP2). At each current density, the presence of gas products from the cathode outlet stream was examined for 15 minutes.

During this time, the volume of the outlet products was measured and then analyzed by an on-line gas chromatograph (990 Micro GC, Agilent). H₂, CH₄, CO were detected in the channel 1 (MS5A SS), while C₂H₄ was detected in the channel 2 (Poraplot U).

Before doing the experiment the calibration of the gas chromatography was carried out using a calibration bottle that contains the principal gases we will study (H₂, CO, C₂H₄, C₂H₆). The calibration data can be seen in Appendix 2.2

The FEx of the X obtained products, such as C_2H_4 , CH_4 , CO and H_2 , were estimated by using the following equation:

$$FE_{x} = \frac{Q_{x}}{Q_{Total}} = \frac{n_{x}N_{x}F}{Q_{Total}}$$
(3)

Where Q_X and Q_{Total} is the charge passed to produce product X and the total passed charge (C) during CO₂RR, n_X represents the electron transfer number of product X, N_X is the product amount (mol) of X measured by the GC, and F is the Faraday constant (96485 C/mol).

6. RESULTS OF THE SCALED-UP CATALYST

6.1. CATALYST CHARACTERIZATION

The best way to scale-up the Cu₂O-5wt.% CeO₂ catalyst was by the mixture of five 1gbatches. By the first method (only increasing 5 times the quantities of the precursor salts) was not possible the catalyst scaling. In this case, a different synthesis reaction behavior was identified when NaOH was added. Particularly, the color of the solution was black brownish when the solution must be orange (See appendix 1). Therefore, taking into consideration this problem, we selected the mixture of batches for the catalyst scaling.

Figure 7 shows the scaled-up Cu₂O-5wt.% CeO₂ catalyst. As can be observed in Figure 7a, nanoparticles with cubic-type shapes were reproduced, according to the used synthesis [14]. It is important to mention that we are looking for this type of morphology because the cubic-type nanoparticles are highly selective to ethylene production.

On the other hand, Cu, Ce and O were the main elements identified by EDS analysis as part of the catalyst composition. In Figure 7b and Figure 7c are show the spectrum and distribution of the main elements, respectively. According to Figure7b, the cerium distribution was not totally homogeneous. There are some cerium oxide particles agglomerated. However, we can improve the agglomeration by increasing the stirring time during the synthesis and before adding the NaOH.



Figure 7: SEM-EDS analysis a) SEM image of the Cu₂O-5CeO₂ at x18,000 (scale bar: $1\mu m$), b) Distribution of the Cu, Ce and O in the elemental mapping , c) EDS Spectrum.

Figure 7c shows the composition of the sample at atomic scale. This data is very useful because it allows to estimate the weight mass percentage corresponding to the copper and cerium phases. In this case, the experimental composition was 75.7 % for Cu and 7.1% for Ce. It was quite higher than the 5% we wanted but it was the best result in the synthesis we have done when trying to scale the experiment. (See appendix 1)

The different behavior of the scaled-up synthesis was because of the different particle size (See Figure 8) and it is the reason this synthesis was rejected. The solution we found for scalingup was prepare five individual synthesis and at the end join all the product, as mentioned before.



Figure 8: SEM for the scaled-up synthesis. At magnification a) x5,000, b) 10,000 (scale bar:1μm)

7. RESULTS OF THE INK OPTIMIZATION AND GAS DIFFUSION ELECTRODE CHARACTERIZATION

7.1. RESULTS OF THE INK OPTIMIZATION

7.1.1. Study of the stability of the ink

Table 2 shows the composition of the 7 evaluated inks.

Table 2: Composition of the inks for the study of their stabilities.

Entry	Weight catalyst [mg]	Nafion© [μL]	Ethanol [µL]	Ratio catalyst/solvent	Ratio nafion/solvent
а	20	140	500	0.0400	0.2800
b	20	140	700	0.0286	0.2000
с	20	140	933	0.0214	0.1500
d	20	140	1400	0.0143	0.1000
е	20	140	1866	0.0107	0.0750
f	20	140	2800	0.0071	0.0500
g	20	140	5000	0.0040	0.0280



Figure 9: Study of different catalyst/solvent and ionomer/solvent ratio at time 0h, 5h, 24h

As it is shown in Figure 9, the most stable vial was the one prepared with 5ml of absolute ethanol, was the one that shows less sedimentation of the catalyst after 24h in observation.

7.1.2. Study of the effect of the solvent

The inks in this part were prepared as it is shown in Table 3.

Entry	Weight catalyst [mg]	Nafion© [µL]	Ethanol [mL]	lsopropanol [mL]	Water [mL]
а	40	280	10	—	—
b	40	280	5	5	_
C	40	280	7	—	3
d	40	280	_	7	3
е	40	280	_	10	_

Table 3: Composition of the inks for studying the effect of the solvent.

Once the ratio of the solvent vs the catalyst has been found we proceed to study which is the best solvent by performing a stability test that can be seen in Figure 10.



Figure 10: a) Ethanol 100% v/v, b) Ethanol- isopropanol 50-50% v/v, c) Ethanol- water 70-30% v/v, d) isopropanol- water 70-30% v/v, e) isopropanol 100% v/v. At time 0h, 5h, 24h

After 24h of the preparation and as it is shown in Figure 10, the vials did not show many differences in the composition. It was identified that vial E, the one prepared using isopropanol, had less deposition, and the one that had more separation was vial C and D.

Sequentially, all the inks were sprayed into the carbon paper support to evaluate their evaporation behavior during the deposition of the catalyst layer.

Ink A was like it supposed to be because it was the initial ink used previously for the research group. When this ink is sprayed into the heated carbon paper ethanol was quickly evaporated without taking much time.

Ink B the solvent was evaporated rapidly but slower than the one with only ethanol.

Ink C and ink D the process of airbrush was slower, water needs more time for evaporation. When it was sprayed one time some drops were observed, and the ink fell down the electrode. So, the best way to spray this ink was to draw a «Z» in the electrode and wait 30-60 seconds until was fully dried.

With ink E the solvent was absorbed easily for the first layers, but when the carbon paper had a thin film of the ink, the solvent needed more drying time.

7.1.3. Gas diffusion electrode characterization

7.1.3.1 Scanning electron microscope

The five inks sprayed on the carbon-paper support of the previous section were then characterized using scanning electron microscope. Figure 11 shows the surface of catalyst layer of the 5 inks at x300. Figure 11c and Figure 11d show big cracks in the surface of the catalyst layer of the electrode, while Figure 11b and Figure 11e show smaller cracks compared to the other two. On the other hand, the ink prepared with ethanol (Figure 11a) as the solvent does not appear any crack in their surface.



Figure 11: Inks at magnification x300 (scale bar:1µm). The solvent of the inks is: a) ethanol, b) ethanol/ isopropanol (50-50%), c) ethanol/water (70-30%), d) isopropanol/water (70-30%), e) isopropanol.

Rugosity may be an interesting surface property because the non-uniform surface can contribute to maintaining local pH during the reaction and stabilizing the faradaic efficiency. So, considering this aspect, the ink prepared with ethanol/isopropanol (Figure 10b) is the one that has

the smoothest surface, followed by ink C and D. Then ink A shows some agglomeration and rugosity. But the roughest surface was ink E (Figure 10e).



Figure 12: Inks at magnification x43,000 (scale bar:100 nm). The solvent of the inks are a) ethanol, b) ethanol/ isopropanol (50-50%), c) ethanol/water (70-30%), d) isopropanol/water (70-30%), e) isopropanol.

Taking a closer look into these inks (see Figure 12) we can see we have cubic particles using the different inks. But we can see a different distribution of the particles, Figures 12c and 12d have holes because of the cracks we can observe in Figures 11c and 11d, in addition the size of the particles varies more than the other inks, this may be caused because of the water that contains the ink.

In Figure 11e we observed some agglomeration caused by the roughness of the surface. This can be due to the smaller particles that had the inks containing isopropanol as a solvent (Figures 12d and 12e). Compared to the inks prepared with ethanol (Figures 12a and 12c) which are

bigger, it even leads to the formation of thin catalyst layers (see Figures 13e and 13b). Maybe a thinner catalyst layer but with more rugosity is better than a larger and smoother layer.



Figure 13:Thickness of the different electrodes observed by Scanning electron microscopy. Magnification x150 (100 nm). The solvent of the inks is: a) ethanol, b) ethanol/ isopropanol (50-50%), c) ethanol/water (70-30%), d) isopropanol/water (70-30%), e) isopropanol.

The catalyst layers deposited with inks containing isopropanol or ethanol/isopropanol (Figures 13b and 13e) were thinner than the ones with only ethanol (Figure 13a) or ethanol/water (Figure 13c). Perhaps a thinner catalyst layer but with more rugosity is better than a larger and smoother layer.

Water appears to not affect the thickness of the layer because Figures 13a and 13c, and Figures 13b and 13d had similar thicknesses. In particular, there was a very broad difference in the thickness of the inks with ethanol and the ones with isopropanol. Isopropanol makes thinner layers (see Figures 13b, 13d, 13e).

From Figure 13 and applying Eq.(1) the thickness of the layer are shown in Table Table 4: Thickness of the catalyst layer

	Carbon paper	а	b	С	d	е
Thickness [µm]	41.83	85.80	86.75	82.73	24.78	45.83

Among all electrodes, the catalyst layer associated with the sample d was thinner than the carbon paper, because probably when the ink was sprayed it was not done uniformly in all the surface and at the edge of the carbon paper the layer was thinner compared to the centre.

In conclusion, isopropanol appears to create rougher surfaces, smaller cubic particles, and a thin catalyst layer, because inks b, d, and e presented thinner layers than a and c, which contain ethanol.

7.1.3.2 Contact angle

This procedure consists of depositing a drop of water on the surface of the catalyst layer and calculating the contact angle between the drop and the surface ink. At a higher contact angle, a more hydrophobic catalyst layer is achieved in the electrode. So, for this project, we are looking for a high contact angle.



Figure 14: Contact angle of the inks deposited on GDE. The solvent of the inks is: a) ethanol, b) ethanol/ isopropanol (50-50%), c) ethanol/water (70-30%), d) isopropanol/water (70-30%), e) isopropanol.

As seen in Figure 14, the catalyst layers with higher contact angle were achieved for ink A (ethanol), ink B (ethanol/isopropanol) and ink E (isopropanol). In contrast, Inks C and D achieved smaller contact angle. This can be linked to the implementation of water as solvent.

Therefore, since inks A, B and E shown potential properties, they were selected to study their performance in the CO₂RR to ethylene. Inks A and B were studied in appendix 3. Ink E was studied in the following sections.

7.3. Study of the effect of PTFE in the ink

The effect of PTFE was finally evaluated for the most promising ink formulation. The electrode corresponding to the ink formulation E was selected due to its efficient electrocatalytic performance, which is detailed in section 8.

In Table 5 is show as the new inks were prepared:

Table 5: Composition of inks used for studying the effect of PTFE.

Entry	Weight catalyst [mg]	Nafion© [µL]	lsopropanol [mL]	PTFE [g]
а	40	280	10	—
b	40	280	10	0.002



Figure 15: Stability at time 0h, 5h, 24h. Solvent: a) Isopropanol, b) isopropanol + PTFE

As shown in Figure 15, the stability of the ink with and without PTFE was similar because past 24h the separation of the catalyst in the two solvents were quite similar. So, PTFE does not affect the stability of the ink.

For spraying the inks, they were sonicated for one hour, and then the solution of the vials was sprayed on carbon paper making two new gas diffusion electrodes, the procedure was the same explained before.

7.3.1 Gas diffusion electrode characterization

7.3.1.1 Scanning electron microscope

Figures 16a and 16d show the transversal section of the electrodes. The thickness of the catalyst layer that contains isopropanol (Figure 16a) was not similar to the one made with isopropanol and PTFE (Figure 16e). This means PTFE promotes the increase in the thickness of the layer. The catalyst layer for isopropanol was near 46 μ m thick, and 68 μ m when PTFE was added on the ink.



Figure 16: SEM images using isopropanol as a solvent at magnification a) x100, b) x300, c) x43,000 (scale bar: 100nm). Ink with isopropanol and PTFE at magnification d) x150, e) x300, f) x43,000 (scale bar:100nm).

From Figures 16b and 16e, we can identify that the surface was rough like we had seen before, but with PTFE appears to have more rugosity (see Figure 16e), so for this property, the GDE with isopropanol with PTFE seems to be better than the one that did not contain PTFE. Furthermore, Figures 16c and 16f show that the addition of PTFE did not modify the cubic shape of the particles.

7.3.1.2. Contact angle

For finishing with characterization, the contact angle was also evaluated with and without PTFE. How is it supposed to be, the gas diffusion electrode containing PTFE in their ink was more hydrophobic because their achieved contact angle (see Figure 17) was bigger than the ink that did not contain PTFE.

So, after the characterization of the gas diffusion electrodes seems that we had two remarkable options to study when doing CO₂ electroreduction.



Figure 17: Contact angles of the gas diffusion electrodes with a) isopropanol, b) isopropanol with PTFE as the solvent

In the following section, we were able to decide which electrode was better or if they were equal for the reduction reaction in converting CO₂ into ethylene.

8. RESULTS OF THE CO₂RR TO C₂H₄

Figure 18 illustrates the faradaic efficiency of the different products obtained during the CO_2 electroreduction of the most promising gas diffusion electrode (ink E using isopropanol as solvent). This was selected due to its competitive ethylene production. Results of the electrochemical activity for ink A and B are shown in Appendix 3. As can be seen in Figure 18, the principal products obtained were ethylene (C₂H₄), carbon monoxide (CO), methane (CH₄), and hydrogen (H₂).

For this gas diffusion electrode, the potentials were negative, which means that we were studding the reduction of carbon dioxide.



Figure 18: Faradaic efficiency and cathode potential as a function of the current density for the gas diffusion electrode prepared with isopropanol.

The best faradaic efficiency for ethylene was 55% at -1.4V and using a current density of -150 mA/cm². At current densities higher than -150 mA/cm², the faradaic efficiencies to carbon monoxide and hydrogen were increased compared to ethylene (see Table 6). The most inefficient reaction condition was -50 mA/cm² because the faradaic efficiency for ethylene achieved was only 21.5% at -0.9V.

Entry	Current density [mA/cm²]	%FE (H2) [%]	% FE (CH4) [%]	% FE (CO) [%]	% FE (C2H4) [%]	Ewe (RHE) [V]
1	- 50	20.2	0.9	57.5	21.5	-0.944
2	-100	16.8	1.2	37.6	44.5	-1.224
3	-150	17.1	0.8	26.1	56.0	-1.434
4	-200	19.8	1.2	24.7	54.3	-1.594
5	-250	20.7	1.1	27.1	51.2	-1.624
6	-300	24.3	1.7	23.4	50.5	-1.764

 Table 6: Faradaic efficiencies and electrode potentials at different current densities for isopropanol gas diffusion electrode

Another thing to notice in Figure 18 is that when the production of ethylene increases, the production of carbon monoxide decreases. This means that the higher production of CO (57.5%) was at -50 mA/cm², and the lowest production (23.4%) was at -300 mA/cm².

For methane the faradaic efficiency remains practically constant, and no dependence was observed between production of these gases with the current density or with the production of ethylene. Hydrogen instead increases their production until 25% at -300 mA/cm².

The results for the second electrode studied (ink made with isopropanol and PTFE) were illustrated in Figure 19.



Figure 19: Faradaic efficiency and cathode potential as a function of the current density for the gas diffusion electrode prepared with isopropanol and PTFE.

In Figure 19 the faradaic efficiency for ethylene was higher compared to Figure 18, thus, the selectivity production to ethylene increases when PTFE was added to the ink. In this case, the efficiency was near 60%. It achieved an increase of 5% compared to the GDE that did not contain PTFE.

The faradaic efficiency for hydrogen (See Table 7) remained the same (near 20%) when PTFE was added. For methane, the faradaic efficiency was increased to 3%. Furthermore, the faradaic efficiency for carbon monoxide decreased until 12% at -300 mA/cm², when without PTFE at the same current the conversion was 23%.

Table 7: Faradaic efficiencies and	potentials at	different d	current o	densities f	or isoprop	anol
and PTFE gas diffusion electrode						

Entry	Current density [mA/cm²]	%FE (H2) [%]	% FE (CH4) [%]	% FE (CO) [%]	% FE (C2H4) [%]	Ewe (RHE) [V]
1	- 50	34.2	1.7	40.9	23.2	-0.869
2	-100	18.7	2.7	36.6	42.0	-1.064
3	-150	19.5	2.9	24.0	53.6	-1.104
4	-200	20.9	3.1	18.0	58.0	-1.214
5	-250	22.7	2.8	14.6	59.9	-1.424
6	-300	25.1	3.2	12.6	59.1	-1.424



Figure 20: Comparison of the hydrophobic behavior of the gas diffusion electrode during CO₂RR. The solvent of the ink is: a) isopropanol, b) isopropanol + PTFE.

In Figure 20 is important to notice that on the left (Figure 20a) some KOH electrolyte drops were passed through the gas diffusion electrode. When PTFE was added to the ink (Figure 20b), the formation of these drops was inferior at the same point of the experiment. It is normal that some flooding occurs when higher current density is applied, but it seems that PTFE lets pass less KOH electrolyte drops through the catalyst layer and the microporous layer.

In summary, adding PTFE improves the conversion of carbon dioxide into ethylene. And makes the gas diffusion electrode more hydrophobic preventing the flow of KOH through the electrode.

9. CONCLUSIONS

In this work, the scaling of the ink formulation for the fabrication of a 5 cm² GDE based on Cu₂O-5wt.%CeO₂ catalyst was investigated for the CO₂RR to ethylene. The catalyst synthesis was scaled-up and the stability of the ink formulation (solvent+ ionomer+ catalyst) with and without PTFE was analyzed using different advanced characterization techniques (SEM and contact angle). Furthermore, the performance of the most promising GDEs were tested using a lab-scale flow cell at different current densities. The following conclusions were found:

- The scale-up of the catalysts was not achieved when the amounts of the precursor salts in the synthesis was increased by 5 times. We identified a different reaction synthesis behavior when NaOH was added to the solution. As an alternative to scale-up the catalyst, we prepared five individual synthesis and join the final product at the end of the reactions. For this proposed batch, the cubic-type morphology and experimental catalyst composition (Cu=78wt.% and CeO₂=7±1wt.%) was verified by SEM-EDS analysis.
- From the ink stability tests, the optimal catalyst/solvent and ionomer/solvent ratios found to an optimal ink formulation for a GDE of 5cm² were 0.0040 and 0.0280, respectively.
- At the optimized ratios, we found the best solvent for the ink was isopropanol. This solvent promoted the formation of a thin catalyst layer with a favorable rough surface, according to SEM-EDS. Furthermore, isopropanol was confirmed as the best solvent for the ink because when testing this gas diffusion electrode, its faradaic efficiency to ethylene (55%) was higher than the faradaic efficiency reported for the rest of the studied inks, which were close to 42%.
- Finally, a GDE with modified hydrophobicity property was achieved by adding PTFE on the ink. We detected that PTFE helped to prevent flooding of potassium hydroxide electrolyte into the electrode. Furthermore, by improving the hydrophobicity, we also increased the faradaic efficiency for ethylene, which was 60%, higher than the GDE that did not contain PTFE.

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11. ACRONYMS AND SYMBOLS

- CFS: Carbonaceous fiber structures
- CL: catalyst layer
- CO₂RR: carbon dioxide electroreduction
- EDS: Energy-dispersive X-ray spectroscopy
- Ewe: Working electrode potential
- FE: faradaic efficiency
- GC: gas chromatograph
- GDE: Gas diffusion electrode
- HER: Hydrogen evolution reaction
- j: current density
- MFC: mass flow channel
- MPL: microporous layer
- PTFE: polytetrafluoroethylene
- RHE: Reversible hydrogen electrode
- SEM: scanning electron microscopy

APPENDICES

APPENDIX 1: SUPPORT INFORMATION



Figure 21.1: Synthesis behavior of the first scaled-up method.



Figure 221.2: SEM-EDS of the synthesis without extra time.

APPENDIX 2: CALIBRATIONS

1. Calibration of the pump

The next table shows the experimental data used for calibration the pump.

Theoretical flow (ml/min)	Volume (mL)	Min	Seconds	Total time (min)	Experimental flow (ml/min)	Experimental flow medium	
	50	9	20	9,33	5,3571		
5	50	9	21	9,35	5,3476	5,35	
	50	9	20	9,33	5,3571		
	50	4	40	4,67	10,7143		
10	50	4	41	4,68	10,6762	10,69	
	50	4	41	4,68	10,6762		
	50	3	8	3,13	15,9574		
	50	3	6	3,10	16,1290	16,01	
15	50	3	8	3,13	15,9574		
15	100	6	14	6,23	16,0428		
	100	6	13	6,22	16,0858	16,04	
	100	6	15	6,25	16,0000		
	100	4	41	4,68	21,3523		
20	100	4	40	4,67	21,4286	21,40	
	100	4	40	4,67	21,4286		
	100	3	45	3,75	26,6667	26,63	
25	100	3	45	3,75	26,6667		
	100	3	46	3,77	26,5487		
	100	3	6	3,10	32,2581		
30	100	3	7	3,12	32,0856	32,14	
	100	3	7	3,12	32,0856		
	100	2	41	2,68	37,2671		
35	100	2	40	2,67	37,5000	37,42	
	100	2	40	2,67	37,5000		
	100	2	21	2,35	42,5532		
40	100	2	21	2,35	42,5532	42,55	
	100	2	21	2,35	42,5532		
	100	2	6	2,10	47,6190		
45	100	2	5	2,08	48,0000	47,87	
	100	2	5	2,08	48,0000		
	100	1	53	1,88	53,0973		
50	100	1	53	1,88	53,0973	53,26	
	100	1	52	1,87	53,5714		



2. Calibration of the gas chromatograph

The next four tables show the residence time and area of the gas obtained in channel 1 or channel 2 when modifying the gas flow that passes through mass flow 1 and 2 (MF1 and MF2):

MF1 100-0% MF2								
		CANAL 1				CANAL 2		
	gas	tR	Area		gas	tR	area	
	H2	0,514	17132		CH4	0,578	776717	
	CH4	1,147	752269		CO2	_	0	
R3	со	2.12	883541		C2H4	0.959	1048970	
					C2H6	1,078	1143739	
	H2	0,514	17214		CH4	0,578	775327	
	CH4	1,147	751077		CO2	-	0	
R4	со	2.12	882613		C2H4	0.959	1047179	
		,			C2H6	1.078	1141143	
	H2	0.514	17150		CH4	0.578	775246	
	CH4	1 147	750438		CO2		0	
R5	0	2 12	882201		C2H4	0.959	1046873	
		2,12	002201		(2114	1 078	1140466	
			ME1 50-	50% ME2	CZTIU	1,078	1140400	
			IVIET 20-	JO70 IVIEZ				
	-	CANAL 1				CANAL 2		
	gas	tR	Area		gas	tR	area	
	H2	0,514	8632		CH4	0,578	374990	
	CH4	1,147	382151		CO2	0,79	51216981	
K3	CO	2,12	440648		C2H4	0,959	503096	
					C2H6	1,078	550491	
	H2	0,514	8383		CH4	0,578	375080	
	CH4	1,147	382701		CO2	0,79	51196779	
R4	CO	2,12	441344		C2H4	0,959	502846	
					C2H6	1,078	550207	
	H2	0,514	8347		CH4	0,578	375014	
	CH4	1,147	381916		CO2	0,79	51206844	
К5	со	2.12	441207		C2H4	0.959	503240	
		,			C2H6	1.078	550230	
			MF1 20-	80% MF2				
		CANAL 1				CANAL 2		
		+P	Aroa			+D	2502	
	ຮaຈ 	0.514	2440		gas CUA	0.579	152122	
		0,514	157020		CO3	0,578	152132	
R3	CO	1,14/	190707		CU2	0,79	01022207	
	0	2,12	180/0/		C2H4	0,959	201935	
	112	0.514	2450		C2Hb	1,078	222185	
	H2 CU4	0,514	3450		CH4	0,578	152973	
R4	CH4	1,14/	15/85/		CU2	0,79	81832410	
	0	2,12	182336		C2H4	0,959	203018	
					C2H6	1,078	223532	
	H2	0,514	3432		CH4	0,578	153181	
R5	CH4	1,147	158100		CO2	0,79	81836756	
	CO	2,12	181474		C2H4	0,959	203227	
					C2H6	1,078	223997	

MF1 10-90% MF2								
	CANAL 1				CANAL 2			
	gas	tR	Area		gas	tR	area	
	H2	0,514	1735		CH4	0,578	76370	
62	CH4	1,147	79457		CO2	0,79	91874431	
N3	CO	2,12	91620		C2H4	0,959	99986	
					C2H6	1,078	110842	
	H2	0,514	1704	ĺ	CH4	0,578	76516	
B 4	CH4	1,147	79609		CO2	0,79	91905206	
64	CO	2,12	91023		C2H4	0,959	100198	
					C2H6	1,078	111128	
	H2	0,514	1703	ĺ	CH4	0,578	76924	
DE	CH4	1,147	79848		CO2	0,79	91892981	
K5	CO	2,12	91829		C2H4	0,959	100736	
					C2H6	1,078	111727	

From the data obtained we proceed into calculating the theoretical area for each gas in channel 1 and channel 2:

CHANNEL 1												
%Gas	ppm H2	Area H2	Area H2 calc	Error	ppm CH4-1	Area CH4-1	Area CH4-1 calc	Error	ppm CO	Area CO	Area CO calc	Error
1	10090	17132	17112,64	0%	10550	752269	755295,6	0%	10430	883541	849711,24	4%
1	10090	17214	17112,64	1%	10550	751077	755295,6	1%	10430	882613	849711,24	4%
1	10090	17150	17112,64	0%	10550	750438	755295,6	1%	10430	882201	849711,24	4%
0,5	5045	8632	8556,32	1%	5275	382151	377647,8	1%	5215	440648	424855,62	4%
0,5	5045	8383	8556,32	2%	5275	382701	377647,8	1%	5215	441344	424855,62	4%
0,5	5045	8347	8556,32	2%	5275	381916	377647,8	1%	5215	441207	424855,62	4%
0,2	2018	3440	3422,528	1%	2110	157020	151059,12	4%	2086	180707	169942,248	6%
0,2	2018	3450	3422,528	1%	2110	157857	151059,12	5%	2086	182336	169942,248	7%
0,2	2018	3432	3422,528	0%	2110	158100	151059,12	5%	2086	181474	169942,248	7%
0,1	1009	1735	1711,264	1%	1055	79457	75529,56	5%	1043	91620	84971,124	8%
0,1	1009	1704	1711,264	0%	1055	79609	75529,56	5%	1043	91023	84971,124	7%
0,1	1009	1703	1711,264	0%	1055	79848	75529,56	6%	1043	91829	84971,124	8%
CHANNEL 2												
CHAININEL Z												
CHAININEL 2												
%Gas	ppm CH4-2	Area CH4-2	Area CH4-2 calc	Error	ppm C2H4	Area C2H4	Area C2H4 calc	Error	ppm C2H6	Area C2H6	Area C2H6 calc	Error
%Gas 1	ppm CH4-2 10550	Area CH4-2 776717	Area CH4-2 calc 770382,1	Error 1%	ppm C2H4 10100	Area C2H4 1048970	Area C2H4 calc 1038280	Error 1%	ppm C2H6 10350	Area C2H6 1143739	Area C2H6 calc 1132807,5	Error 1%
%Gas 1 1	ppm CH4-2 10550 10550	Area CH4-2 776717 775327	Area CH4-2 calc 770382,1 770382,1	Error 1% 1%	ppm C2H4 10100 10100	Area C2H4 1048970 1047179	Area C2H4 calc 1038280 1038280	Error 1% 1%	ppm C2H6 10350 10350	Area C2H6 1143739 1141143	Area C2H6 calc 1132807,5 1132807,5	Error 1% 1%
%Gas 1 1 1	ppm CH4-2 10550 10550 10550	Area CH4-2 776717 775327 775246	Area CH4-2 calc 770382,1 770382,1 770382,1	Error 1% 1% 1%	ppm C2H4 10100 10100 10100	Area C2H4 1048970 1047179 1046873	Area C2H4 calc 1038280 1038280 1038280 1038280	Error 1% 1% 1%	ppm C2H6 10350 10350 10350	Area C2H6 1143739 1141143 1140466	Area C2H6 calc 1132807,5 1132807,5 1132807,5	Error 1% 1% 1%
%Gas 1 1 1 0,5	ppm CH4-2 10550 10550 10550 5275	Area CH4-2 776717 775327 775246 374990	Area CH4-2 calc 770382,1 770382,1 770382,1 385191,05	Error 1% 1% 1% 3%	ppm C2H4 10100 10100 10100 5050	Area C2H4 1048970 1047179 1046873 503096	Area C2H4 calc 1038280 1038280 1038280 519140	Error 1% 1% 1% 3%	ppm C2H6 10350 10350 10350 5175	Area C2H6 1143739 1141143 1140466 550491	Area C2H6 calc 1132807,5 1132807,5 1132807,5 566403,75	Error 1% 1% 1% 3%
%Gas 1 1 0,5 0,5	ppm CH4-2 10550 10550 10550 5275 5275	Area CH4-2 776717 775327 775246 374990 375080	Area CH4-2 calc 770382,1 770382,1 770382,1 385191,05 385191,05	Error 1% 1% 1% 3% 3%	ppm C2H4 10100 10100 10100 5050 5050	Area C2H4 1048970 1047179 1046873 503096 502846	Area C2H4 calc 1038280 1038280 1038280 519140 519140	Error 1% 1% 1% 3% 3%	ppm C2H6 10350 10350 10350 5175 5175	Area C2H6 1143739 1141143 1140466 550491 550207	Area C2H6 calc 1132807,5 1132807,5 1132807,5 566403,75 566403,75	Error 1% 1% 1% 3% 3%
%Gas 1 1 0,5 0,5 0,5	ppm CH4-2 10550 10550 10550 5275 5275 5275	Area CH4-2 776717 775327 775246 374990 375080 375014	Area CH4-2 calc 770382,1 770382,1 770382,1 385191,05 385191,05 385191,05	Error 1% 1% 3% 3% 3%	ppm C2H4 10100 10100 10100 5050 5050 5050	Area C2H4 1048970 1047179 1046873 503096 502846 503240	Area C2H4 calc 1038280 1038280 1038280 519140 519140 519140	Error 1% 1% 1% 3% 3% 3%	ppm C2H6 10350 10350 10350 5175 5175 5175	Area C2H6 1143739 1141143 1140466 550491 550207 550230	Area C2H6 calc 1132807,5 1132807,5 1132807,5 566403,75 566403,75 566403,75	Error 1% 1% 3% 3% 3%
%Gas 1 1 0,5 0,5 0,5 0,2	ppm CH4-2 10550 10550 5275 5275 5275 5275 2110	Area CH4-2 776717 775327 775246 374990 375080 375014 152132	Area CH4-2 calc 770382,1 770382,1 385191,05 385191,05 385191,05 154076,42	Error 1% 1% 3% 3% 3% 1%	ppm C2H4 10100 10100 5050 5050 5050 2020	Area C2H4 1048970 1047179 1046873 503096 502846 503240 201935	Area C2H4 calc 1038280 1038280 519140 519140 519140 207656	Error 1% 1% 3% 3% 3% 3%	ppm C2H6 10350 10350 5175 5175 5175 5175 2070	Area C2H6 1143739 1141143 1140466 550491 550207 550230 222185	Area C2H6 calc 1132807,5 1132807,5 1132807,5 566403,75 566403,75 566403,75 226561,5	Error 1% 1% 3% 3% 3% 2%
%Gas 1 1 1 0,5 0,5 0,5 0,5 0,2 0,2	ppm CH4-2 10550 10550 10550 5275 5275 5275 5275 2110 2110	Area CH4-2 776717 775327 775246 374990 375080 375014 152132 152973	Area CH4-2 calc 770382,1 770382,1 385191,05 385191,05 385191,05 154076,42 154076,42	Error 1% 1% 3% 3% 3% 1% 1%	ppm C2H4 10100 10100 5050 5050 5050 2020 2020	Area C2H4 1048970 1047179 1046873 503096 502846 503240 201935 203018	Area C2H4 calc 1038280 1038280 519140 519140 519140 207656 207656	Error 1% 1% 3% 3% 3% 3% 2%	ppm C2H6 10350 10350 5175 5175 5175 5175 2070 2070	Area C2H6 1143739 1141143 1140466 550491 550207 550230 222185 223532	Area C2H6 calc 1132807,5 1132807,5 1132807,5 566403,75 566403,75 566403,75 226561,5 226561,5	Error 1% 1% 3% 3% 3% 2% 1%
%Gas 1 1 1 0,5 0,5 0,5 0,5 0,2 0,2 0,2	ppm CH4-2 10550 10550 5275 5275 5275 2110 2110 2110	Area CH4-2 776717 775327 775246 374990 375080 375014 152132 152973 153181	Area CH4-2 calc 770382,1 770382,1 770382,1 385191,05 385191,05 385191,05 154076,42 154076,42	Error 1% 1% 3% 3% 3% 1% 1%	ppm C2H4 10100 10100 5050 5050 5050 2020 2020 20	Area C2H4 1048970 1047179 1046873 503096 502846 503240 201935 203018 203227	Area C2H4 calc 1038280 1038280 519140 519140 519140 207656 207656 207656	Error 1% 1% 3% 3% 3% 3% 2% 2%	ppm C2H6 10350 10350 5175 5175 5175 2070 2070 2070	Area C2H6 1143739 1141143 1140466 550491 550207 550230 222185 223532 223997	Area C2H6 calc 1132807,5 1132807,5 1132807,5 566403,75 566403,75 566403,75 266403,75 226561,5 226561,5 226561,5	Error 1% 1% 3% 3% 3% 2% 1%
%Gas 1 1 1 0,5 0,5 0,5 0,5 0,2 0,2 0,2 0,1	ppm CH4-2 10550 10550 5275 5275 5275 2110 2110 2110 1055	Area CH4-2 776717 775327 775246 374990 375080 375014 152132 152973 153181 76370	Area CH4-2 calc 770382,1 770382,1 385191,05 385191,05 385191,05 154076,42 154076,42 154076,42 77038,21	Error 1% 1% 1% 3% 3% 3% 1% 1% 1% 1%	ppm C2H4 10100 10100 5050 5050 5050 2020 2020 20	Area C2H4 1048970 1047179 1046873 503096 502846 503240 201935 203018 203227 99986	Area C2H4 calc 1038280 1038280 519140 519140 207656 207656 207656 103828	Error 1% 1% 3% 3% 3% 3% 2% 2% 2% 4%	ppm C2H6 10350 10350 5175 5175 5175 2070 2070 2070 2070 1035	Area C2H6 1143739 1141143 1140466 550491 550207 550230 222185 223532 223997 110842	Area C2H6 calc 1132807,5 1132807,5 566403,75 566403,75 566403,75 226561,5 226561,5 226561,5 113280,75	Error 1% 1% 3% 3% 3% 2% 1% 1% 2%
%Gas 1 1 0,5 0,5 0,5 0,5 0,2 0,2 0,2 0,2 0,1 0,1	ppm CH4-2 10550 10550 5275 5275 5275 2110 2110 2110 1055 1055	Area CH4-2 776717 775327 775246 374990 375080 375014 152132 152973 153181 76370 76516	Area CH4-2 calc 770382,1 770382,1 385191,05 385191,05 385191,05 154076,42 154076,42 154076,42 154076,42 77038,21	Error 1% 1% 1% 3% 3% 3% 1% 1% 1% 1% 1%	ppm C2H4 10100 10100 5050 5050 2020 2020 2020 20	Area C2H4 1048970 1047179 1046873 503096 502846 503240 201935 203018 203227 99886 100198	Area C2H4 calc 1038280 1038280 519140 519140 207656 207656 207656 103828	Error 1% 1% 3% 3% 3% 2% 2% 2% 4% 3%	ppm C2H6 10350 10350 5175 5175 5175 2070 2070 2070 1035 1035	Area C2H6 1143739 1141143 1140466 550491 550207 550230 222185 223532 223997 110842 111128	Area C2H6 calc 1132807,5 1132807,5 566403,75 566403,75 566403,75 226561,5 226561,5 226561,5 113280,75	Error 1% 1% 1% 3% 3% 2% 1% 1% 2% 2%

Then we plot area vs ppm for each gas for completing the calibration:





Doing the experiments, we saw that we obtain more quantity of carbon monoxide, and the calibration was under range. So, we repeat the calibration using a new calibration bottle that had 10% of CO.

ppm CO	Area CO	Area CO calc	Error
100000	8138655	8146800	0%
100000	8142285	8146800	0%
100000	8145720	8146800	0%

Note: the graph above corresponding to CO has the modification explained.

APPENDIX 3: STUDY OF CO₂RR ETHANOL AND ETHANOL/ISOPROPANOL GDE

1. CO₂ electroreduction

We studied the performance of these GDE at the same condition described before.



Figure 23: The faradaic efficiency and reduction potential as a function of the current density for the gas diffusion electrode prepared with Ethanol.

 Table 8: The faradaic efficiency and reduction potential as a function of the current density for the gas diffusion electrode prepared with Ethanol.

Entry	Current density [mA/cm²]	%FE (H₂) [%]	% FE (CH₄) [%]	% FE (CO) [%]	% FE (C ₂ H ₄) [%]	Ewe (RHE) [V]
1	- 50	31.75	0.78	62.69	4.78	-0.514
2	-100	23.75	1.23	51.68	23.35	-0.524
3	-150	21.31	0.86	39.31	38.51	-0.644
4	-200	28.11	1.77	32.47	37.65	-0.704
5	-250	40.13	2.31	26.54	31.02	-0.824
6	-300	37.03	2.60	28.83	31.55	-0.894

Figure 21 illustrated the faradaic efficiency and reduction potential for the GDE made with ethanol. From Table 8 we can observe that the best faradaic efficiency for ethylene was 38% when the current density was -150 mA/cm². And at higher densities the FE decreased because the electrode stopped working.

In Figure 22 we can see how GDE made with ethanol and isopropanol worked. In this case we obtained more faradaic efficiency for ethylene compared with the previous. But from Table 9 the faradaic efficiency for ethylene is near 54% at -200 mA/cm². And when applying higher densities, the electrode didn't stopped working. Apparently having isopropanol in the ink increased the FE. So this was the reason why we studied the ink with only isopropanol and isopropanol with PTFE



Figure 24: The faradaic efficiency and reduction potential as a function of the current density for the gas diffusion electrode prepared with ethanol/isopropanol.

Table 9: The faradaic efficiency and reduction potential as a function of the current
density for the gas diffusion electrode prepared with ethanol/isopropanol.

Entry	Current density [mA/cm²]	%FE (H ₂) [%]	% FE (CH₄) [%]	% FE (CO) [%]	% FE (C ₂ H ₄) [%]	Ewe (RHE) [V]
1	- 50	23.90	1.28	59.39	15.43	-0.644
2	-100	21.29	4.15	41.17	33.39	-0.804

3	-150	19.45	1.80	31.16	47.59	-1.014
4	-200	19.96	2.21	24.53	53.30	-1.264
5	-250	24.18	4.30	21.79	49.73	-1.384
6	-300	28.89	7.43	19.63	44.05	-1.394