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# ASSESSMENT OF $CO_2$ ELECTROVALORIZATION TO VALUE ADDED PRODUCTS: INFLUENCE OF THE POTENTIAL ON DMC ELECTROSYNTHESIS

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| **TÍTULO** | **Assessment of $CO_2$ electrovalorization to value added products: Influence of the potential on DMC electrosynthesis** | | |
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## PALABRAS CLAVE/KEYWORDS

Carbon dioxide; valorization; dymethil carbonate; methanol; ionic liquid.

## PLANTEAMIENTO DEL PROBLEMA/SCOPE

Carbon dioxide is one of the main contributors to greenhouse effect. Several strategies are being studied to mitigate $CO_2$ emissions (Aresta et al., 2014). Among them, $CO_2$ valorization into value added products is being considered as an interesting alternative solution (Qiao et al., 2014). Dimethyl carbonate (DMC) is an environmentally friendly chemical of great interest, used in multiple applications and also as gasoline octane booster. DMC traditional routes implied the use of hazardous phosgene and CO, which encourages the interest of developing new processes (Yuan et al., 2009). Among them, the electrochemical synthesis of DMC from methanol and $CO_2$ is particularly interesting. The aim of this work is to evaluate a $CO_2$ electrovalorization process for the synthesis of dymethil carbonate using ionic liquid [bmim][Br] and $CH_3OK$ and study the influence of the potential on the formation of DMC product. Several experiments have been conducted at different potentials, and the results have been analyzed and compared with the results of previous work (Garcia-Herrero et al., 2014) in terms of DMC and sub-products formation.

## RESULTADOS /RESULTS

The electrosynthesis of DMC from MeOH and $CO_2$ avoiding cancerogenic agents has been studied. Experiments up to 6h have been conducted. The potential difference from 3.5 to 5.5V has been studied. From the analysis of the liquid phase the desired product DMC and DME as by-product has been detected. The results show that the potential applied has a significant influence on the process. When 3.5V and 4V potentials were applied no relevant differences were obtained. However, increasing the potential from 4.5V to 5.5V resulted in a higher production of DMC.

Moreover the kinetic analysis for the formation of DMC has been performed. A zero-order kinetic for the five different potentials studied has been obtained. The reaction rates and kinetic constants are reported (k=880 $mmol\cdot m^{-2}\cdot h^{-1}$ for 5.5V). Substantial improvements in terms of DMC production are achieved by increasing potential difference from 3.5V (7.97 $mmol\cdot L^{-1}$) to 5.5V (25.52 $mmol\cdot L^{1}$).

## CONCLUSIONES / CONCLUSIONS

The results of this work confirm that the use of undivided cell is favorable in the formation of DMC product. Moreover, increasing the potential applied between 4.5V and 5.5V results in higher concentration of DMC. The increase in the potential also gives higher rate of product formation. Further research is required to optimize the different variables involved in the process.

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# 1. INTRODUCTION

## 1.1 Social Challenges: Water and Energy

The 21st century is a century full of challenges on a global scale. There are several environmental problems to face like climate change, global warming, loss of biodiversity, weakening of the ozone layer, acid rain or deforestation. Also our civilization is built using a very high energy demand. The actual challenge is to decrease the fossil fuel dependency that has caused big environmental problems, and move, as possible, to renewable sources.

Another big problem is the availability of fresh water. Although water covers 70.9% of the Earth's surface, only 3% of the Earth's water is freshwater and around 99% of this is locked in polar ice and groundwater. Therefore, less than 1.0% of all freshwater (≈0.01% of total global water) is available for people and ecosystems (IPCC, 2013). The use of membranes for desalination of drinking water is a very promising technology to alleviate this need.

## 1.2 $CO_2$ emissions and dependency on fossil fuels.

Greenhouse effect has attracted attention in the last years because of its undesirable effect on global warming and climate change. The atmospheric abundance of carbon dioxide ($CO_2$), which is the most notorious anthropogenic greenhouse gas, was 390.5 ppm in 2011, which is 40% greater than in 1750. Since the IPCC fourth assessment report in 2005, $CO_2$ has increased by 11.7 ppm and future estimates foresee that this growth in $CO_2$ concentration will continue (IPCC, 2013). In an ideal scenario, $CO_2$ produced should be the same as $CO_2$ consumed, therefore $CO_2$ level would remain constant to maintain environmental stability (Qiao et al., 2014). As a consequence of these greenhouse emissions, global mean temperature has increased about 0.8º in the last century and a half (IPCC 2013). The World Energy Outlook (2013) warns that even taking into account the impact of measures already announced by governments to improve energy efficiency, support renewables, reduce fossil-fuel subsidies and, in some cases, to put a price on carbon, energy-related $CO_2$ emissions still rise by 20% to 2035. This leaves the world on a trajectory consistent with a long-term average temperature increase of 3.6°C, far above the internationally agreed 2°C target (International Energy Agency, 2013).

Energy production is the dominating source of anthropogenic greenhouse gases emissions. In 2006, over 28 billion tons of $CO_2$ were emitted due to fossil fuel consumption. Around 57% of all global anthropogenic GHGs derive from fossil fuel combustion, with energy supply as the largest contributing sector (Höök et al., 2010). The main sources of $CO_2$ emissions are: electricity, transportation, and industry. One of the options to reduce these emissions is to switch from fossil fuels to renewable sources. However, because of their intermittent nature, the fraction of energy that can be supplied from renewable sources will be limited to 30% (Jhong et al., 2013).

Fossil fuels have been the driving force behind the industrialized world and its economic growth and will probably continue to do so for a long time. Currently, almost 80% of the energy used by mankind comes from fossil fuels, with oil accounting for 32.8%, coal for 27.2% and natural gas for 20.9%. According to The World Energy Outlook (2013) the energy generated from fossil fuels will remain the major source and is still expected to meet about 80% of energy demand in 2035, following current policies. If new policies are applied, then this estimation is reduced to 75%, and in the 450 scenario (in which the concentration of $CO_2$ reaches 450 ppm) the dependency is then 63%. Only 0.8% of the world’s primary energy is derived from geothermal, wind, solar or other alternative energy sources.

In this context, alternative technologies have been proposed in the last years: to capture and geologically sequestrate $CO_2$, or to convert $CO_2$ into useful low carbon fuels (Qiao et al., 2014).

### 1.3 New Alternatives for $CO_2$. Capture. Monoethanolamine (MEA) and membranes.

Some of the possible options for $CO_2$ capture are: (i) pre-combustion, capture from the reformed synthesis gas of an up-stream gasification unit; (ii) post-combustion, capture from the flue gas stream after combustion (Li et al., 2013) and (iii) oxyfuel combustion, which is a modified post-combustion method where fuel is combusted in almost pure oxygen instead of air (Olajire, 2010). There are various ways of doing the $CO_2$ capture: by using membranes, a physical or chemical absorbent and a solvent. Among these technologies, chemical absorption using aqueous alkanolamine solutions is proposed to be the most applicable technology for $CO_2$ capture before 2030 (Yu et al., 2012).

Physical absortion is an operation based on Henry's Law. $CO_2$ is absorbed under high pressure and low temperature, and desorbed at reduced pressure and increased temperature. Typical adsorbents are dimethylether, propylene glicol, metanol, methylpyrrolidone and propylene carbonate, which are used in different commercial processes. There are currently existing commercial processes such as Selexol Process, Rectisol Process, Purisol Process, Morphysorb Process, and Fluor process (Olajire, 2010).

Chemical absorption processes usually consist of an absorber and a stripper in which the absorbent is thermally regenerated. The flue gas containing $CO_2$ enter a packed bed absorber from the bottom and contacts counter-currently with a $CO_2$-lean absorbent. After absorption, the $CO_2$-rich absorbent flows into a stripper for thermal regeneration. After regeneration, the $CO_2$-lean absorbent is pumped back to the absorber for cyclic use. The pure $CO_2$ released from the stripper is then compressed (Yu et al., 2012). This technology has several advantages such that it is the most mature technology and it is already commercialized for several decades. Moreover, it is suitable for adaptation in existing power plants. On the other hand, it has a few drawbacks such as high equipment corrosion rate, the amine degradation by $NO_2$, $SO_2$ and $O_2$ entering in the flue gas (which causes economic, operational, and environmental problems), large equipment size and high energy consumption. The most common absorbents used for $CO_2$ capture are alkanolamines. The amine group of these alkanolamines can be monoethanolamine (MEA), diethanolamine (DEA) and N-methyldiethanolamine (MDEA).

Another alternative is $CO_2$ capture by chemical or physical adsorption. Physical adsorption uses a physical adsorbent. Some of the most commonly used adsorbents are activated carbon and zeolites. There are also other possible and promising adsorbents like mesoporous silica or metal organic frameworks. By using a chemical adsorbent, like amine-based adsorbents, we find as an advantage the low heat of regeneration over aqueous amines due to the low heat capacity of solid supports. There are also amine-impregnated supports as important adsorbents. In general, in order to develop an appropriate capture adsorbent, it should satisfy: low-cost raw materials, low heat capacity, fast kinetics, high $CO_2$ adsorption capacity, high $CO_2$ selectivity and thermal, chemical, and mechanical stabilities (Yu et al., 2012) .

Membrane-based technologies for $CO_2$ capture show great advantages over other systems. Three main systems can be considered as the basis of membrane processes for $CO_2$ separation: i) non-dispersive contact via a microporous membrane (mostly focused on postcombustion capture); ii) gas permeation, mainly by using dense membranes (mostly for pre-combustion capture); and iii) supported liquid membranes (pre-combustion and post-combustion capture are both targets) (Luis et al., 2012). There is still a lot of research to be done to achieve industrial implementation of these technologies. Membranes that enhance the process efficiency are needed and there is a little information on how those membranes will be in terms of effectiveness at industrial scale under industrial conditions. Also the membrane stability versus cost is an important drawback.

### 1.4 Novel processes for $CO_2$ recovery: electrovalorization.

One approach to reduce emissions that has gained a lot of attention in the last years is carbon capture and sequestration (CCS). The captured $CO_2$ is stored in deep ocean underground in geological formations such as depleted oil and gas reservoirs. This approach has the potential for reducing the amount of carbon dioxide in the atmosphere but has several issues. As the $CO_2$ must be transported from the source to the sequestration site, it is required that this place is as near as possible to the source, which in some cases is not feasible, with consequent high energy requirements for pumping. Also it has other limitations like the high cost; the intensive energy requirements for separation and housing, the uncertainty about the permanence time of stored $CO_2$ in sites, the impact of large volumes of $CO_2$ on natural systems and also the lack of social acceptance (Aresta et al., 2014; Radgen et al., 2013).

In this context, $CO_2$ valorization is being considered as an interesting alternative solution. As an important advantage, valorization gives a valuable product. As an example of this fact, the obtention of ethanol from $CO_2$ as an alternative to petrochemistry appears promising as it has a double advantage of reusing $CO_2$ while sparing fossil resources and avoiding $CO_2$ emissions from their use. All those technologies generate value-added carbonaceous products such as: fuels, fertilisers, materials and chemicals (Olajire et al., 2013). The main products being studied are, formic acid, methanol, carbon monoxide, ethylene, ethanol, oxalic acid, methane formaldehyde, dimethyl ether (DME) and dimethyl carbonate (DMC).

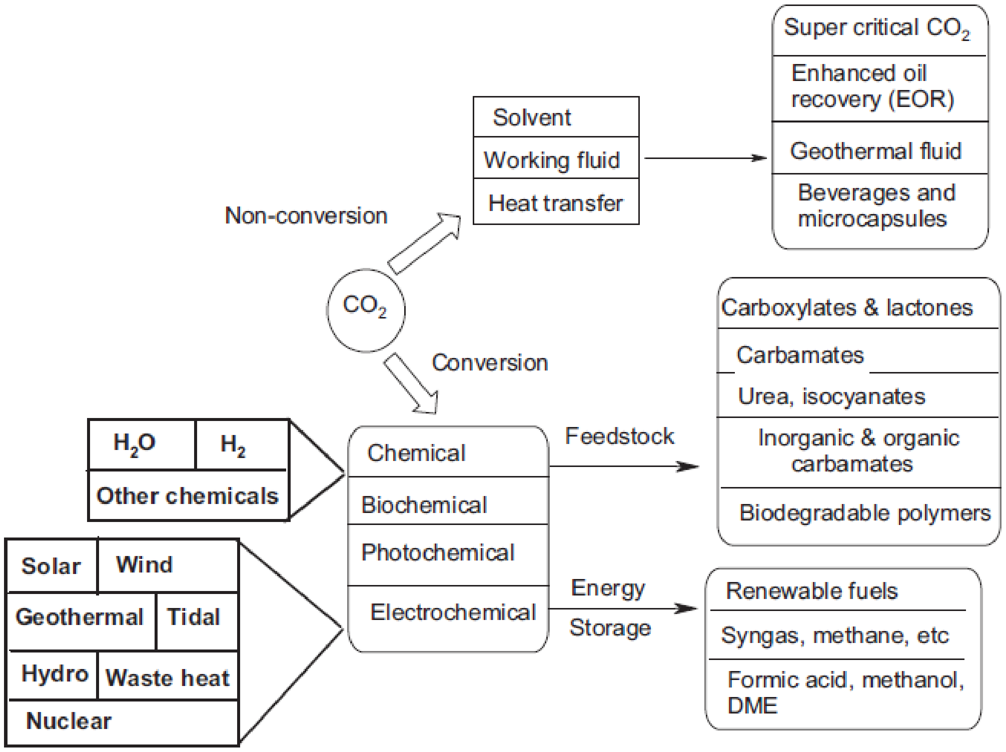

Figure 1. Different pathways for carbon dioxide valorization (Olajire et al., 2013)

As shown in figure 1, $CO_2$ can be valorized as:

1) A storage medium for renewable energy.

2) A feedstock for various chemicals.

3) A solvent or working fluid.

Among the different methods to convert $CO_2$ into value added products, the electrochemical approach has gained a lot of attention. As advantages, it has the possibility of using water as the proton source, requires low temperature of operation, generally intrinsic high faradaic efficiency and the production of pure oxygen as a by-product. Other advantages include that the process is controllable by electrode potentials and reaction temperature, the supporting electrolytes can be recycled so that the overall chemical consumption can be minimized to simply water or wastewater, the electricity needed can be obtained from renewable sources so no new $CO_2$ is generated, and the electrochemical reaction systems are compact, modular, on demand, and easy for scale up applications (Qiao et al., 2014; Yamamoto et al., 2002). The use of electricity from renewable sources seems to be a very special advantage because it provides a way to intermittent renewable power sources to store their energy until they can supply larger portions of energy (Whipple et al., 2010). The electrochemical reduction of $CO_2$ is particularly interesting as it can really contribute to cycle large volumes of $CO_2$ and to store electric energy. Excess electric energy (e.g., energy produced out of peak hours) could be conveniently converted into chemical energy (fuels) to be used in cars (substituting fuels produced from fossil carbon) or for regenerating electric energy during the peak hours. Chemicals such as methanol or gasoline have an energy density that is from 10 to even 100 times higher than that of batteries (Aresta et al., 2014).

### 1.4.1 Direct electroreduction of carbon dioxide

In the electrochemical valorization of $CO_2$, two different broad ways can be distinguished: i) direct conversion of $CO_2$ into products; ii) electrosynthesis of different products in which $CO_2$ is one of the reagents.

There are different products of electrochemical $CO_2$ reduction, including CO, formate, methane, ethylene, ethanol, n-propanol, allyl alcohol, acetaldehyde, propionaldehyde, acetate, methanol,ethylene glycol, glycolaldehyde, hydroxyacetone, acetone, and glyoxal.

In an electrolytic cell, $CO_2$ is reduced on the cathode while the oxygen evolution reaction (OER) takes place on the anode. Some examples of half reactions of the cathode for electrochemical $CO_2$ reduction into products are shown below:

$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$

$CO_2 + H^+ + 2e^- \rightarrow HCOO^-$

$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$

$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O$

Four different types of metal catalysts have been identified for $CO_2$ reduction in aqueous solution (Jhong et al., 2013):

- Metals that mainly form formic acid, HCOOH ( Pb, Hg, In, Sn, Cd, Tl).
- Metals that mainly form carbon monoxide, CO (Au, Ag, Zn, Pd , Ga).
- Metals that form significant amounts of hydrocarbons such as methane and ethylene (Cu).
- Metals that mainly form hydrogen (Pt, Ni, Fe, Ti) .

#### 1.4.1.1 Nanomaterials used as catalysts

The most commonly explored electrocatalysts for $CO_2$ electroreduction are transition metals elements and their associated compounds, such as metal complexes. This is probably because these metals have vacant orbital and active d electrons, which are believed to energetically facilitate the bonding between the metal and $CO_2$ and also facilitate the desorption of the reduction products (Qiao et al., 2014).

Metal nanoparticles have attracted a great interest in scientific research and industrial applications, owing to their unique large surface-to-volume ratios and quantum-size effects. Since industrial catalysts usually work on the surface of metals, the metal nanoparticles, which possess much larger surface area per unit volume or weight of metal than the bulk metal, have been considered as promising materials for catalysis.

Some of the interesting properties that shown these catalyst nanoparticles are listed below (Dragomir, 2009):

- **Large surface area to volume ratio** as compared to the bulk equivalents (high contact area)
- **Large surface energies** to facilitate the reaction mechanism.
- **The transition** between molecular and metallic states providing specific electronic structure local density of states.
- **Plasmon excitation.** Useful for describing propagation of energy, if the level of plasmon excitation is high, the propagation of energy is going to be high too.
- **Quantum confinement**. The confinement of electrons in the nano-scale dimensions results in quantization of energy and momentum, and reduced dimensionality of electronic states.

- **Short range ordering.** The position of the short-range order peaks confirmed the successful linking of the bridging ligands of particles.
- **Large number of low coordination** sites such as corners and edges, having a large number of dangling bonds and consequently specific and chemical properties and the ability to store excess electrons.

In particular, Ag nanoparticles are becoming an increasingly important material in many technologies. They exhibit the highest efficiency of plasmon excitation. Besides, Ag is the only metal in which plasmon resonance can be tuned to any wave length in the visible spectrum. The main product in the electroreduction of $CO_2$, using Ag or Au cathodes, is CO. Ag shows good current efficiency for this purpose. It is efficient and selective. As has been studied by Salehi-Kojin et al. (2013), the particle size of Ag nanoparticles in $CO_2$ electroreduction is the most important property to have in mind. They found that the catalytic activity increases with decreasing particle size until a certain particle size, here, 5 nm, and that the activity drops when going to even smaller nanoparticle size (1 nm). To choose the right size of the nanoparticles must be one of the most important decisions to make.

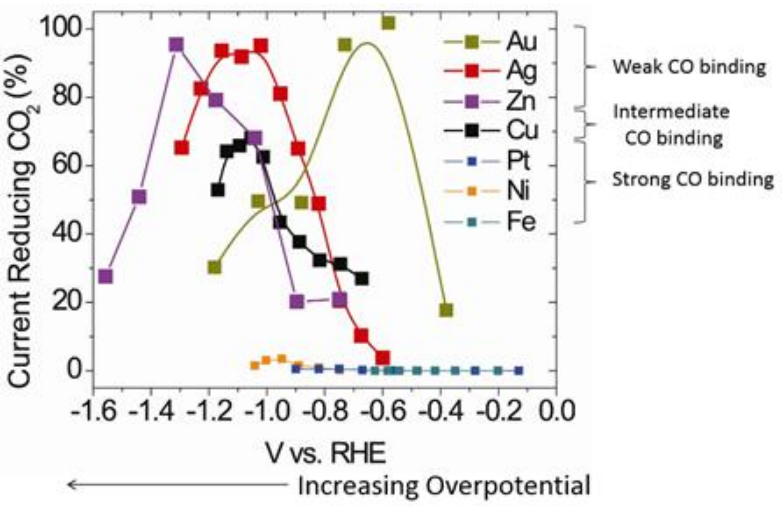

Figure 2. Several metals in the electroreduction of $CO_2$ (Khul, 2012)

### 1.4.1.2 Gas Diffusion Electrodes (GDE's)

The Gas Diffusion Electrodes (GDES) are multicomponent and gas porous matrices. A GDE is generally composed of a reaction layer and an accessorial layer (the gas diffusion layer or GDL). The GDL, adjacent to the catalyst layer and the flow field, plays an important role in GDE performance and has several functions (Zhang, 2008):

- Transportation of reactants: The GDL should be able to provide reactant pathways from the flow field channels to the catalyst layer and uniformly distribute the reactants onto the whole reaction surface.
- Transportation of liquid water: The GDL offers pathways for liquid water removal from the catalyst layer to the flow channels.
- Conduction of electrons: the GDL allows electron transfer from the bipolar plate to the catalyst layer or viceversa.
- Mechanical support.
- Heat conduction: the GDL should be able to effectively remove the produced heat from the catalyst layer.

The GDL has a thinner microporous layer (MPL) as illustrate in figure 3.

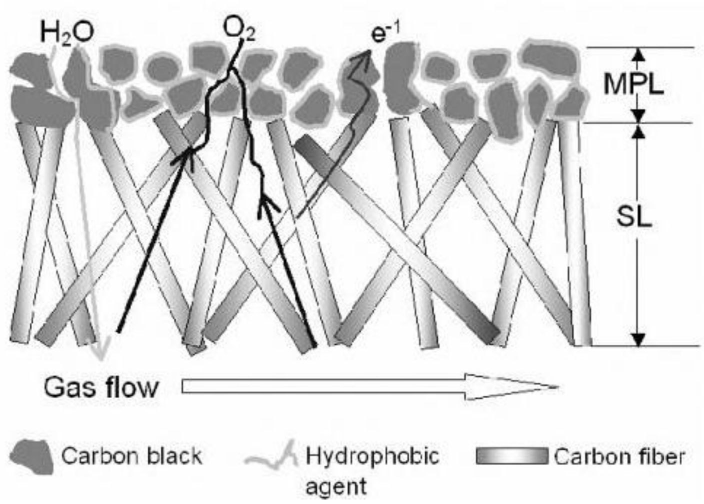

Figure 3. Schemastic diagram of a dual-layer cathode gas diffusion layer (Zhang, 2008)

Contemporary gas diffusion electrodes (GDEs) make use of high-surface area supports for metal catalysts, as well as solid inert materials with high gas permeability. Figure 4 shows a scheme of a GDE consisting of carbon black and PTFE pushed against a porous current collector. The gas can either pass through tortuous pores in the assembly or within the Teflon support. The hydrophobic PTFE inhibits aqueous solutions from completely penetrating the structure but the carbon black support is still capable of being wetted by the electrolyte. Although direct electrochemistry on a gaseous species is still limited by the gas-liquid solubility, the solution layer can be thought of as a thin meniscus and thus capable of supporting very high gas flux rates.

For the fuel cell program, one additional advancement involved the elimination of the liquid electrolyte. Thus, whole electrolyte assemblies consisting of porous electrodes and ion-exchange polymers were manufactured. These assemblies are variously called "MEAs" for membrane electrode assembly, "SPEs" for solid-polymer electrolyte, or "PEMs" for proton exchange membrane. These three acronyms refer to the use of an ionically conducting membrane as an integral element in a device.

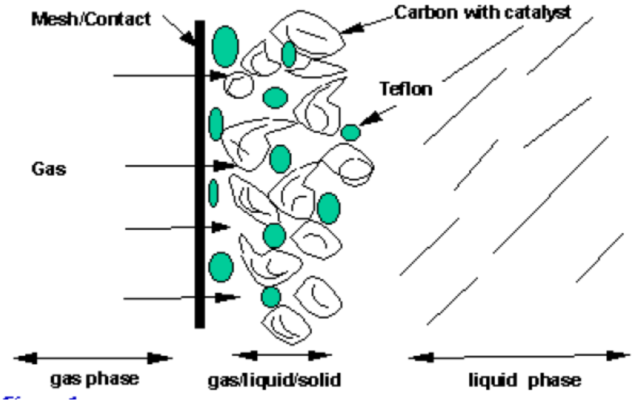

Figure 4. Schemastic representation of a Gas Diffusion Electrode (Castro, 1997)

### 1.4.1.3 Examples of nanomaterials used for electrochemical reduction of $CO_2$

Several works have shown that nanoparticles on catalysts increase $CO_2$ conversion per unit surface area several times in comparison to bulk particles. Relevant examples will be briefly discussed in this section.

The first example proposed of the use of nanoparticles in GDE´s is the use of silver nanoparticle catalyst showing enhanced activity in the $CO_2$ electrolysis (Saleji-Khojin et al., 2013). In this work they show that the rate of $CO_2$ conversion per unit surface area is about 10 times higher on 5 nm silver nanoparticles than on bulk silver. This enhancement disappears at 1nm particles and the explanation they offer is there could be a volcano effect associated with changes of the binding energy of key intermediates as the particle size decreases. In the electrochemical experiments each catalyst sample was deposited onto a clean silver substrate, baked to remove organic impurities, and then soaked in acid or ionic liquid solution to remove metallic impurities. They used X-ray photoelectron spectroscopy to assure the cleaning of the samples. Then, the samples were loaded into a standard 3 electrode cell for the measurements. Also, they used an ultraviolet photoelectron spectroscopy. In the flow apparatus used catalysts were painted onto carbon paper and mounted in a 2 compartment cell. Dried ionic liquid flowed through the cathode compartment, while 0.5 M sulphuric acid flowed into the anode. Voltage was applied to the cell, and the CO and hydrogen production were measured with a gas chromatograph. Both the cathode and the anode were GDE electrodes. Each electrode was backed by aluminum current collectors. The aluminum current collector also served as a gas flow chamber to supply $CO_2$, while the anode was open to the atmosphere for oxygen to escape.

Another example of the use of nanoparticles as catalysts in GDE's is the system proposed by Whipple et al. (2010). In this case, they use a microfluidic reactor for the reduction of $CO_2$ to formic acid using several catalysts. The cell used was a Poly (methyl metacrylate) sheet with a 0.5x2 cm window placed between two gas diffusion electrodes (GDEs). On the cathode side, the catalyst was applied only to the first 1.5 cm. The rest was covered with a poly (tetrafluoroethylene) filter in order to let oxygen bubbles scape and in this way, the electrolyte do not contact the catalyst.

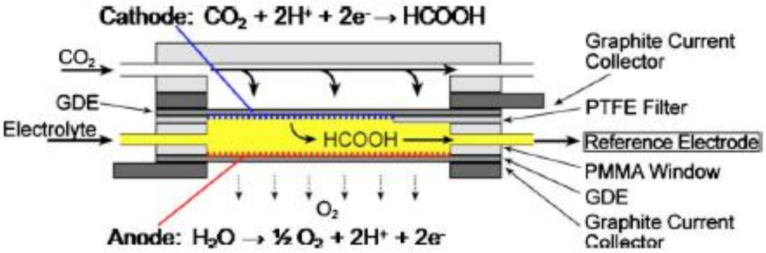

Figure 5. Diagram of the microfluidic reactor used (Whipple et al., 2010)

A suspension of catalyst and Nafion binder was made by sonicating with a 50/50 mixture of water and isopropyl alcohol, which was then painted on the GDE followed by hot-pressing. The cathodes consisted of 2 or 5 $mg \cdot cm^{-2}$ catalyst and 0.1 $mg \cdot cm^{-2}$ Nafion. The anode was 2 $mg \cdot cm^{-2}$ Pt black with 0.1 $mg \cdot cm^{-2}$ Nafion.

Ru–Pd was chosen as a cathode catalyst because it has a high faradaic efficiency for formic acid and low overpotential. A commercial Sn nanopowder was used for comparison.

### 1.4.2 Electrosynthesis of different products using carbon dioxide as reactant

Apart from direct electrochemical reduction of $CO_2$, other interesting possibilities for valorization is the use of $CO_2$ as reactant, together with other species to electrosynthesize products of interest. $CO_2$ can be used in the synthesis of many chemicals.

New electrochemical processes for synthesis of cyclic carbonates from $CO_2$ and diols using ionic liquids have been studied in the last years. Room temperature ionic liquids (RTILs) have held great promise in the development of green chemical applications and processes. For their special physical and chemical properties, such as high thermal stability, negligible vapor pressure, nonflammable, large electrochemical windows and high conductivity, RTILs have been recognized as advantageous alternatives to volatile organic solvents in organic synthesis, catalysis, extraction process, especially in electrochemical applications (Wang et al., 2011).

#### 1.4.2.1 Synthesis of dymethil carbonate (DMC)

Dimethyl carbonate has gained a lot of attention. It can be used as an environmentally benign substitute for highly toxic phosgene and dimethyl sulphate in carbolynation and methylation reactions. It can also be used as a monomer for several types of polymers and as an intermediate in the synthesis of pharmaceutical and agricultural chemicals. DMC can also be used as an octane booster (Dandan et al., 2009; Yuan et al., 2012). The utilization of carbon dioxide, a readily available, inexpensive and environmentally acceptable starting material, has been widely investigated as a raw material for DMC synthesis. However, the direct synthesis process remains insufficient and impractical for industrial applications due to the thermodynamic stability and kinetic inertness of $CO_2$. Electrochemical techniques can solve this problem by providing the preliminary activation of carbon dioxide that is required in the synthetic process (Dandan et al., 2009).

The reaction equation of the DMC synthesis from carbon dioxide is the following:

$$2\mathrm{C}H_3OH(l) + CO_2(g) \rightarrow DMC(l) + H_2O(l)$$

As an example, the model reaction scheme for the production of DMC from $CO_2$ and methanol for the specific case of $CeO_2$-$ZrO_2$ used as solid solution and DMP is illustrated in figure 6.

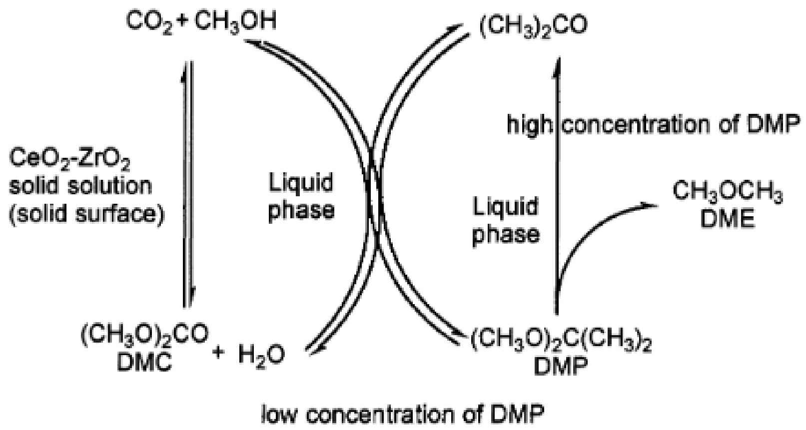

Figure 6. Scheme for the synthesis of DMC from carbon dioxide and methanol (Tomishige et al., 2002)

The use of ionic liquids is getting special interest in the electrochemical valorization of $CO_2$ field. Several works using [bmim][$BF_4$] have been reported proving that this ionic liquid can act as a medium for $CO_2$ reduction and that the reduction of $CO_2$ is easier using ionic liquids than organic solvents (Sun et al., 2011). Different functionalized ionic liquids for the electrochemical conversion of $CO_2$ into DMC have been studied. The most useds are: [Bmim][OH], [apmim][Br],[bmim][Br],[bmim][$BF_4$] and [acmim][Cl]. As additives and co-catalyst several authors have used methyl iodide, propylene oxide, or benzyl chloride using (NPC-Pt) and (NPC-Ag) as nanoporous copper electrodes and achieving high yield values. However, all these additives are toxic and carcinogenic (Garcia-Herrero et al., 2014). Yuan et al. (2009) conclude that $CH_3OK$ is the most effective co-catalyst achieving 3.9% yield of DMC in liquid with [bmim][Br] as a supporting electrolyte. This process is greener and avoids the use of carcinogenic and toxic compounds. Garcia-Herrero et al. (2014) also studied the behaviour of a $CO_2$ valorization process for the electrosynthesis of DMC using [bmim][Br] and $CH_3OK$ under mild conditions showing that [bmim][Br] is not merely an electrolyte and the presence of both the ionic liquid and $CH_3OK$ in the system is required to obtain the desired product.

### 1.5 Limitations and technological challenges

A few limitations are presented such as the high cost of $CO_2$ capture, separation, purification and transportation; the high energy for $CO_2$ chemical/electrochemical conversion; the limitations in market size and investment incentives; the lack of industrial commitment to enhance $CO_2$-based chemicals; and insufficient socio-economic driving forces (Qiao et al., 2014).

There are also several technological challenges in $CO_2$ electrocatalytic reduction. The low catalyst activity makes the overpotential in $CO_2$ electroreduction too high so energy efficiency is not good. Also, there is insufficient catalyst stability and durability. This is because the catalyst becomes gradually covered by reaction intermediates and by-products blocking catalyst active sites. Research in development of new electrocatalyst should be done to palliate these drawbacks, including composite catalyst materials and nanostructured catalyst materials. We also need further fundamental understanding of the process, understanding the fundamentals of the mechanisms of $CO_2$ electroreduction and their relationship to catalyst active site structures and composition (Qiao et al., 2014). On the other hand, to scale-up these processes, some efforts on optimizing system designs and the electrode/reactor should be made.

## 1.6 Objectives. Evaluation of $CO_2$ electro-valorization processes to obtain value added products.

The objective of this work is to evaluate a $CO_2$ electro-valorization process for the synthesis of DMC from methanol using the ionic liquid [bmim][Br] and $CH_3OK$ and continue the study from previous works (Garcia-Herrero et al., 2014) providing further knowledge about the influence of operational variables like the potential difference on the formation of product. For this purpose, several experiments have been conducted at different potentials, and the results have been analyzed and compared with previous results in terms of DMC and sub-products formation.

# 2. METHODOLOGY

## 2.1 Materials

Methanol (Panreac, PA-ACS-ISO, 99.8%), potassium methoxide (Sigma-Aldrich, 95%), 1-butyl-3-methylimidazolium bromide [bmim][Br] (IoLiTec, 99%), nitric acid (Panreac, 65%), carbon dioxide (99.7%) purchased from Air Liquide, dimethyl carbonate (Sigma-Aldrich, anhydrous, >99%) and 2-propanol (Sigma-Aldrich, anhydrous, 99.5%).

## 2.2 Experimental Set-up

A filter press electrochemical cell (Micro Flow Cell®) supplied by ElectroCell was used. Cathode and anode electrodes consist of a Pt/Nb plate (99.5% Pt) with a surface area of 10 cm$^2$. A reference electrode was placed very close to the working electrode surface. This kind of cell enables the operation in two different configurations: (i) divided configuration in which the cell is divided by a membrane in cathode and anode compartments and (ii) undivided cell. As represented in figure 7, in this work the cell is not divided by any membrane.

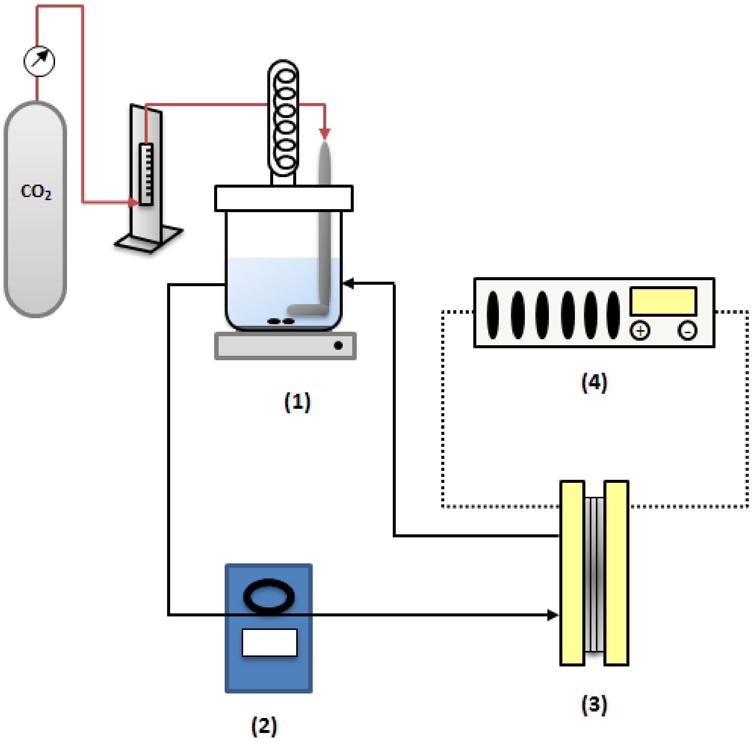

Figure 7. Diagram of the experimental set-up: (1) storage tank, (2) peristaltic pump, (3) filter-press electrochemical cell, (4) potentiostat/galvanostat. Adapted from Garcia-Herrero et al. (2014).

A sealed glass tank was used containing the electrolyte solution with the ionic liquid. The tank was stirred and heated at 303 K. A circulating bath (Polyscience AD07R-20-A12E) was used at 277K to prevent methanol losses. Also, a cooler was placed at the top of the tank to condense the gases. The solution was circulated using a peristaltic pump (AD07R-20-A12E) with a flow rate of 20 mL min$^{-1}$. A septum device was placed at an output of the tank to enable sampling. A rotameter controlled $CO_2$ flowrate entering the system. Figure 8 shows the actual system used in the laboratory.

A portable meter (Hach Q30d Portable) was used to measure pH and temperature. Potential difference was measured using a digital multimeter (Mastech MY-64). The experiments were carried out under potentiostatic conditions using a potentiostat/galvanostat AutoLab PGSTAT 302 N (Metrohm, Inc.). The equipment was controlled by General Purpose Electrochemical System (GPES) software.

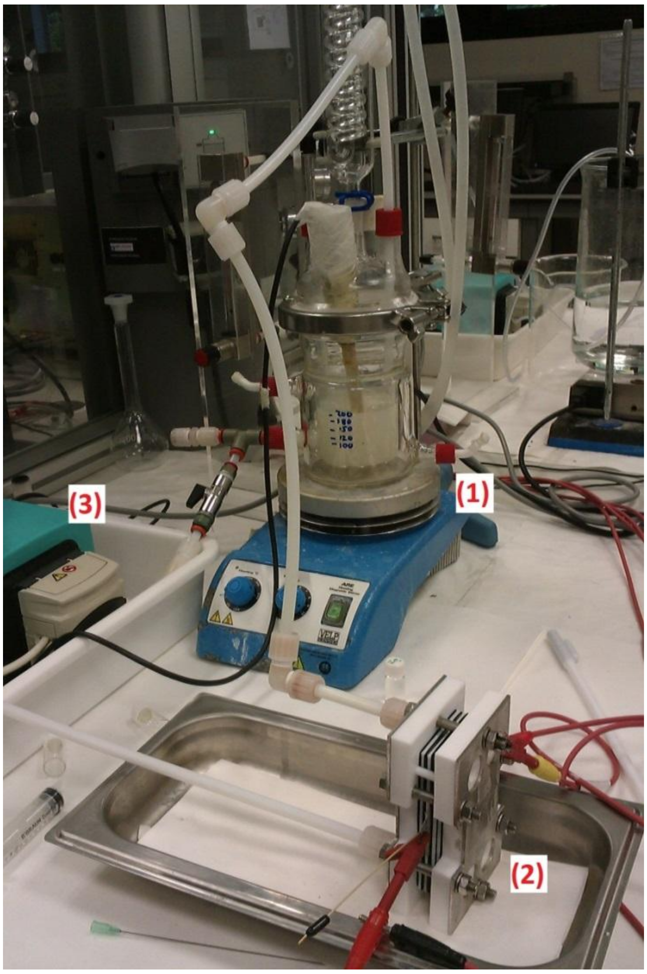

Figure 8. Experimental set-up: (1) Storage tank; (2) Filter press electrochemical cell, connected to the galvanostat; (3) peristaltic pump.

## 2.3 Experimental procedure

The electrodes were cleaned to remove surface adherences using a nitric acid solution at 11%, and then treated with ultra-pure water. The tank, the tubes and also the electrodes were also homogenized with methanol using a syringe for this purpose. Previously, they were cleaned using water, ultra-pure water and air.

The compositions (wt %) for $CH_3OK$, [bmim][Br] and MeOH were the same for all the experiments ($CH_3OK$ 5%, [bmim][Br] 15% and MeOH 80%) because in previous works it has been noted that it is the best performing combination (Garcia-Herrero et al., 2014). For this, 200 ml of methanol solution was prepared, 11 g of potassium methoxide was weighed and also 30 g of [bmim][Br]. All was transferred to the tank, stirred and heated at 303K.

$CO_2$ was bubbled for 20 minutes. A first sample was taken at initial time when $CO_2$ bubbling was stopped. The electrodes were then connected to the potentiostat and the corresponding potential to be studied was then applied. Different potentials, in the range of 3.5-5.5 V, in several experiments, were applied in order to study the influence of the potential in the formation of the product and by-products. The samples were collected every hour and a half and the experiments were conducted up to 6h. The volume of all samples was 4 mL.

## 2.4 Analytical measurement

The products in the liquid phase were analyzed by gas chromatography-mass spectrometry (GC-MS, Agilent Technologies, 6890 N, 5975B), using a 60 m x 250 µm x 1.40 µm DB-624 capillary column (J&W Scientific). The system was equipped with an HP 7694 E Headspace Sampler (Agilent Technologies) and 2-propanol was used as internal standard.

The samples were diluted 1:25 since the GC-MS equipment does not allow highly concentrated solutions. All the diluted samples had a volume of 5ml, of which 4.8 ml was methanol (MeOH), 0.2 ml corresponded to the original sample and 127 µl were internal standard (2-propanol). Samples were measured in duplicated (Figure 9).

Figure 9. Samples prepared for analysis by GC-MS

Standards were also prepared with the aim of developing a calibration method. Dilutions 1:25 were carried out. For this purpose, the standards ranged from 5 ppm to 100 ppm of DMC. 2-propanol was used as internal standard. The standards were analyzed using GC-MS. The output of the chromatograph is a chromatogram, where the x-axis represents the retention time that a particular anolyte takes to pass through the system and the y-axis represents the signal intensity corresponding to the response created by the anolytes. This signal is represented as a peak whose area is proportional to the amount of anolyte detected. For each standard, DMC/IS area ratio is calculated and plotted against the concentration of DMC in ppm. Thus, when analyzing samples, knowing the area ratio of DMC/IS for each sample it is possible to obtain the corresponding concentration of DMC in ppm. Figure 10 shows the calibration curve performed for the quantification of DMC obtained in the subsequent experiments.

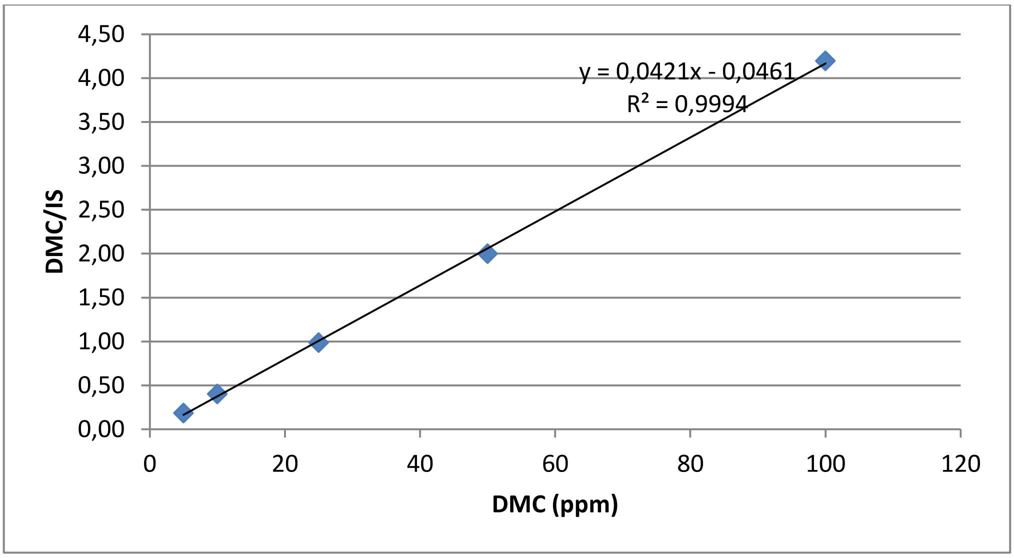

Figure 10. Experimental calibration curve

This technique also allows qualitatively knowing and detecting if some sub-products (DMM, DME, OC or another) are formed.

# 3. RESULTS AND DISCUSSION

## 3.1 Products identified

The main product detected during the gas chromatography-mass spectrometry (GC-MS) analysis was DMC. DME was also detected as by-product. In addition, in previous experiments, a very little presence of other by-products was also observed. Those compounds were: dimethoxymethane (DMM) and tetramethyl orthocarbonate (OC).

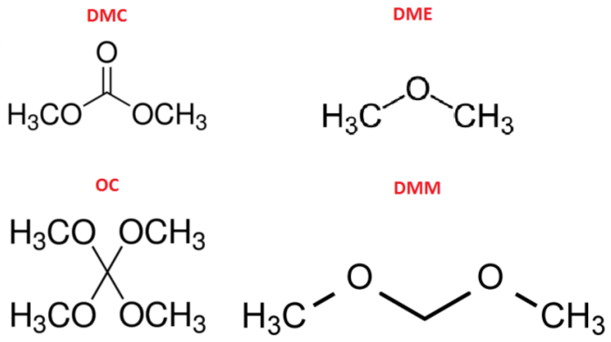

Figure 11. Sub-products identified in previous works by Garcia-Herrero et al. (2014)

In previous works (Garcia-Herrero et al., 2014), all these sub-products were observed after 6 hours of reaction (Figure 11). Also, they can only be mostly appreciated if the experiment is carried out with a cell divided by a membrane. Several experiments were carried out with divided cell with a Nafion 117 membrane and without divided cell. All the experiments were carried out in a very similar system with the same electrolyte compositions (15wt% [bmim][Br], 5wt% $CH_3OK$ and 80wt% MeOH) as in the experiments performed in this work. Figure 12 shows the results of experiments using divided cell carried out in Garcia-Herrero et al. (2014) work, compared to the experiment at 5.5V carried out in this work with undivided cell. DMC concentration increases almost linearly in all cases studied. In no case DMM or OC were detected before six hours of reaction time.

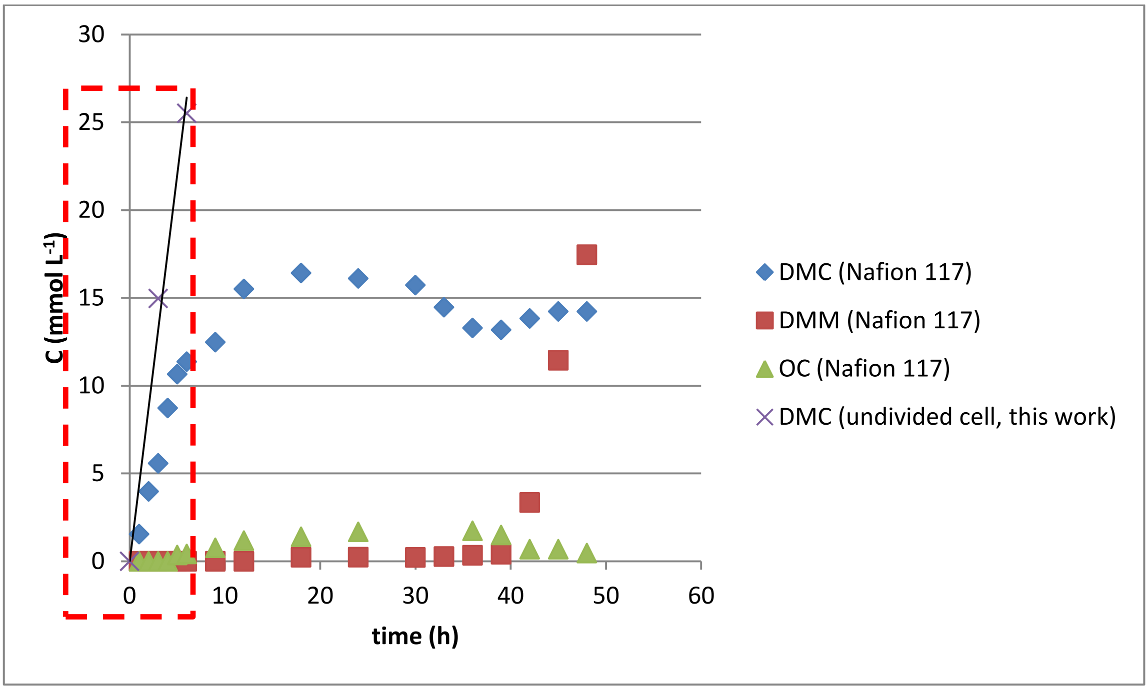

Figure 12. Experimental subproducts observed in previous works and comparison with current results .Adapted from Garcia-Herrero et al. (2014).

The red box indicates the area of special interest in this work because it delimits product formation in the first six hours. As can be observed, with undivided cell much more desired product (DMC) is generated. Moreover, in the first 6h studied, no other products were detected with the exception of DME and some trace compounds. For detailed information about which products are formed after 6h, longer experiments should be carried out. However, the aim of this work is to study the influence of the potential on the formation of DMC product using undivided cell, since it has been shown that in this cell configuration the desired product can be obtained in higher concentrations. Moreover, the results obtained in this work confirmed that, during the initial 6h of the process, the main product obtained is DMC and only DME is obtained as by-product.

Figure 13 shows, as example, the chromatograph results for the experiment carried out at 4V. The first peak that can be seen corresponds to carbon dioxide. Second peak is DME, which is the main by-product detected. DMC is the last peak, being the desired product. Some trace compounds can also be observed. Similar chromatograms were obtained at the rest of cell potentials considered in this work.

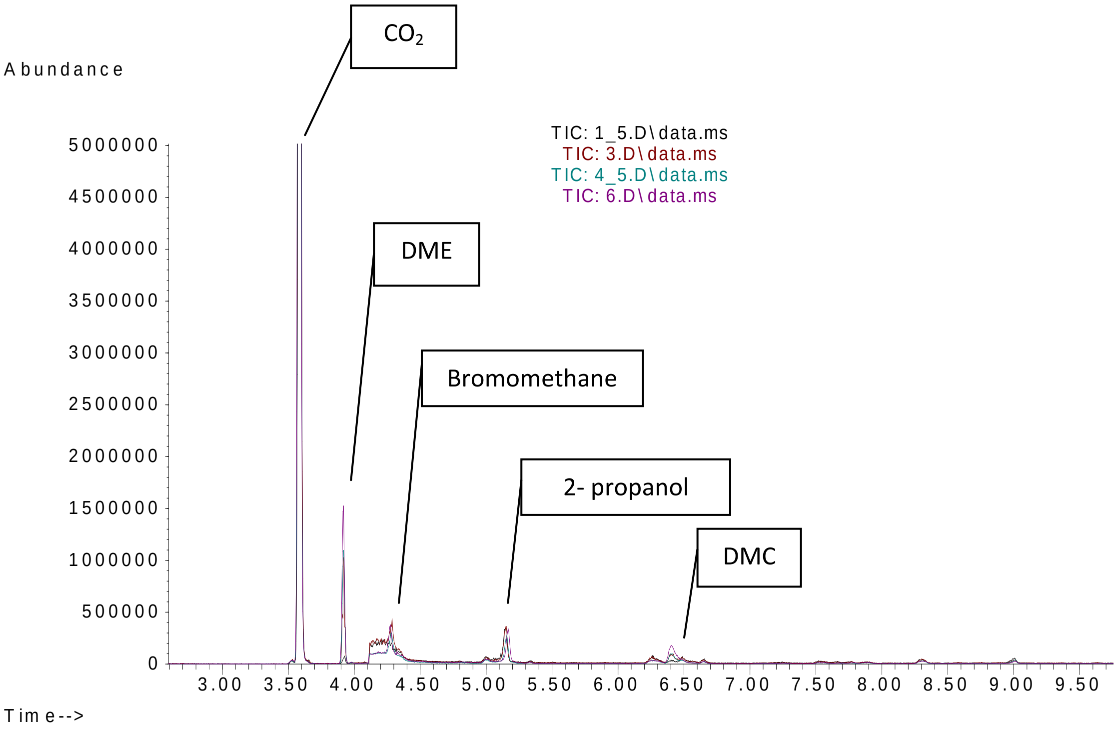

Figure 13. Representation of the results obtained in the chromatograph for the experiment carried out at 4V

### 3.2 Influence of potential on DMC formation

Figure 14 shows the evolution of the average concentration of DMC with the reaction time for the different cases studied. For the 6h of reaction time studied, there is almost a linear increase in the DMC concentration with time, regardless the potential applied. In order to obtain the value of the maximum concentration that could be achieved ($C_{DMC,max}$ ) it could be interesting to do longer experiments. From the studies up to 6h of duration it is not possible to find out which value of $C_{DMC,max}$ would be obtained for each potential. However, the $C_{DMC,max}$ obtained for 5.5V should be higher than the $C_{DMC,max}$ value obtained for the experiments conducted at lower potentials , if we attend the tendency in the formation of DMC shown in figure 14. The data obtained are not exactly a straight line due to the inherent variability associated to an electrochemical system. However, the trend of the data is to increase linearly as has been observed in previous experiments.

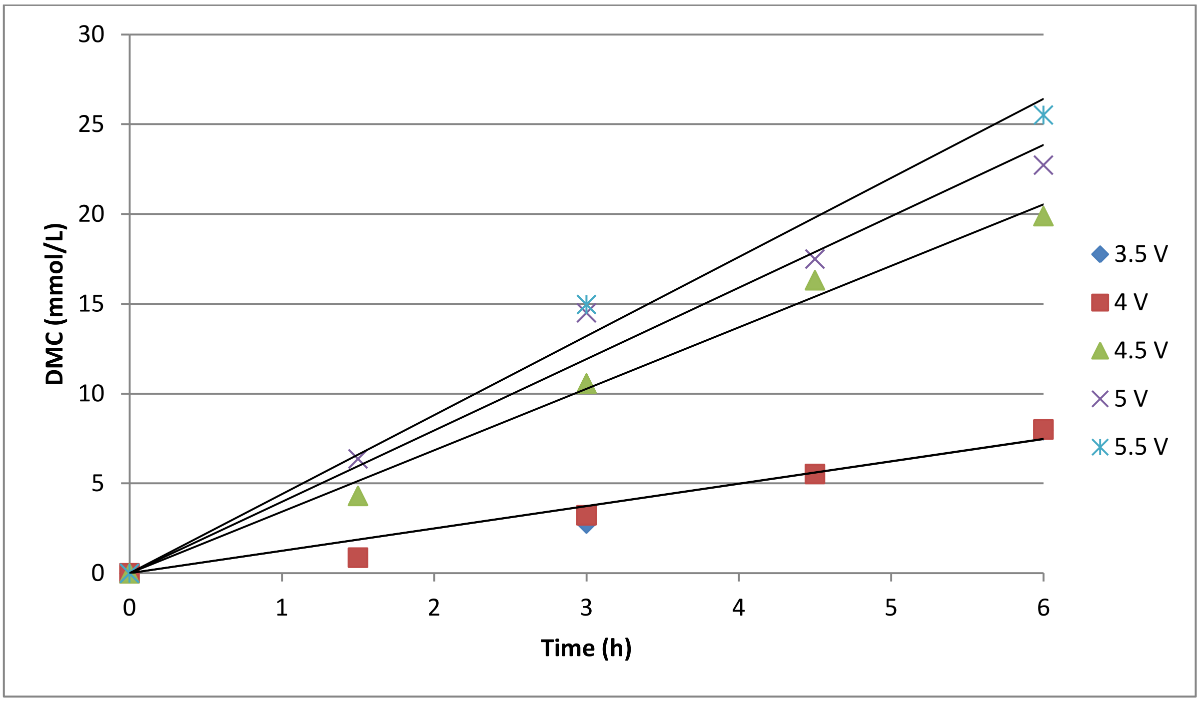

Figure 14. Evolution of DMC concentration with reaction time for the different potential differences studied

Figure 14 shows that in the 5.5V experiment the slope in the evolution of $C_{DMC}$ vs time was higher than in the rest of the experiments ($C_{DMC,6h}$=25.52 mmol·$L^{-1}$) . This means that the rate of DMC formation is higher as will be discussed later. Using the lowest potentials considered (3.5V and 4V), DMC concentration was very low, with no significant difference observed between 3.5V and 4V (7.97 mmol·$L^{-1}$ and 8.01 mmol·$L^{-1}$ up to 6h, respectively). For the experiments carried out, the increase from 3.5V to 4.5V does not seem to be influential in the formation of DMC. However, for higher potential values than 4V it seems to be very significant in the formation of product, since the concentrations achieved were much higher (19.89 mmol·$L^{-1}$ up to 6h for 4.5V case, more than two times the concentration achieved for 4V). Increasing the applied potential, higher DMC concentration is achieved, although only slight increases were observed for potentials higher than 4.5V (22.73 mmol·$L^{-1}$ up to 6h for 5V applied and 25.52 mmol·$L^{-1}$ up to 6h for 5.5V applied).

Therefore, the great improvement seemed to be when changing the potential from 4V to 4.5V. Increasing the potential beyond 4.5V resulted in higher DMC concentrations, but not as much as from 4V to 4.5V.

### 3.3 Influence of potential on DMC formation kinetics

Using the experimental data from the experiments at different cell potentials, a kinetic analysis of DMC formation is then carried out using the differential method. Hence, according to Levenspiel (1986), the methodology followed was as follows:

1) A kinetic equation was supossed. From previous experiences it can be expected that before 6h the concentration versus time increases almost linearly so a zero-order equation where the reaction rate is equal to a constant was then supposed.
2) Concentration vs time data from the experiments were obtained and plotted.
3) Continuous curve fitted to the plotted points was drawn. In the studied cases the data fit on a straight line.
4) The slope of the line was determined. The slope $dC_A/dt$ is the reaction rate.
5) f(C) was evaluated for each concentration
6) $-(dC_A/dt)$ was represented versus f(C). If a straight line through the origin is obtained, the supposed kinetic equation agrees with the data. Otherwise, another kinetic equation has to be tested. Whole procedure can be summarized in Figure 15:

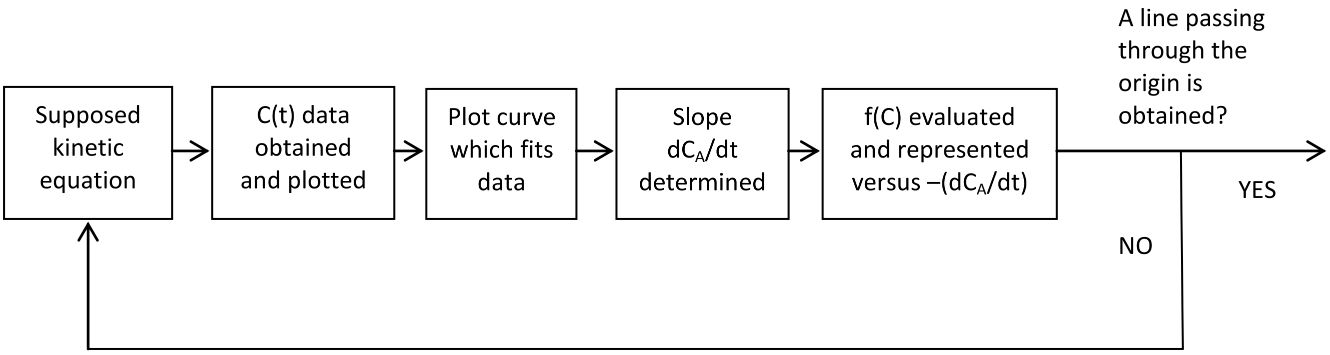

Figure 15. Methodology followed in the kinetic analysis of DMC formation

The rate of reaction of DMC formation ($r_{DMC}$) can be defined as (Garcia-Herrero et al., 2014):

$$r_{DMC} = \frac{1}{A}\frac{dn_{DMC}}{dt} = \frac{V}{A}\frac{dC_{DMC}}{dt}$$

Where $n_{DMC}$ is the number of DMC moles formed, V the volume of electrolyte (0.2 L) and A the electrode area (10 cm$^2$). The kinetic expression is referred to the electrode area since the reaction is assumed to take place on its surface or in the very close adjacent fluid layer (Garcia-Herrero et al., 2014).

For the period of time studied (6h) the concentration vs time data obtained were fitted to the following expression:

$$C_{DMC} = C_{DMC,0} + kt$$

Where $C_{DMC}$ is the concentration of DMC given in mmol·L$^{-1}$, $C_{DMC,0}$ the concentration of DMC at initial time, which is zero, and k is the reaction rate coefficient given in mmol·L$^{-1}$·h$^{-1}$. This expression correspond to a zero-order kinetic, meaning that the rate of the reaction is a constant.

In the different tests carried out at different cell potentials, the rate of DMC formation keeps constant for every value of DMC concentration, resulting the representation as a line parallel to the x axis. The same representation is given when the rate of DMC formation is plotted versus time. This is characteristic of a zero-order reaction. Thus, the expression of the rate of DMC formation in the period of time studied (6h) can be simplified as:

$$r_{DMC} = k$$

For both the representation of the rate of DMC versus DMC concentration and the representation of the rate of DMC versus time, the data from 3.5 V and 4 V are very close each other. This means that the reaction rate for both experiments are almost the same (249.46 mmol·m$^{-2}$h$^{-1}$ and 248.72 mmol·m$^{2}$·h$^{-1}$). However, for the 5.5 V experiment the reaction rate is much higher (880.14 mmol·m$^{-2}$h$^{-1}$), and there is also an increase in the values of the constants as the potential increases. The results of the kinetic analysis for the different potentials are summarized in Table 1.

Table 1. Kinetic analysis results

| Potential difference (V) | Integrated kinetic expression (k given in mmol $L^{-1}$ $h^{-1}$) | k (mmol·$m^{-2}$·$h^{-1}$) |
|---|---|---|
| 3.5 | $C_{DMC} = 1247.3t$ | 249.46 |
| 4 | $C_{DMC} = 1243.6t$ | 248.72 |
| 4.5 | $C_{DMC} = 3420.7t$ | 684.14 |
| 5 | $C_{DMC} = 3973.1t$ | 794.62 |
| 5.5 | $C_{DMC} = 4400.7t$ | 880.14 |

It is important to note that this kinetic study has been carried out considering only 6h of reaction time. Only the start of the reaction was considered so the kinetics results in a zero-order reaction since the concentration of DMC versus time increases in a linear way. This process was studied by Garcia-Herrero et al. (2014) but considering 48h of reaction time. The kinetics change then if a higher time is considered resulting in a different reaction rate, that could be expressed as:

$$r_{DMC} = k_0 - k_1 \cdot C_{DMC}$$

When methanol is in excess, which corresponds to the first hours of the reaction, it can be assumed a zero-order reaction, and the dependency results in a constant value $k_0$. The second term represents the DMC degradation rate due to secondary reactions. As the degradation rate is proportional to the concentration of DMC obtained, in the first hours this term will be negligible when compared to the first term. This is consistent with the results obtained for the first 6h studied, as the reaction rate is a constant and a zero-order reaction can be assumed.

### 3.3 Evolution of the current density

From the experimental results obtained in this work, a study about the evolution of current density versus time was carried out. In consecutive experiments, different potential differences were applied. This results in different current intensities, recorded with the potentiostat/galvanostat, meaning that different values of the flow of electrons through the cell are obtained.

It is logical to expect that in those experiments where a higher potential difference was applied to the electrodes, the current intensity values were also higher. All the experiments used the same electrodes and cell configuration with an area of electrode of 10 $cm^2$. Therefore, all the intensity values obtained during the course of the experiments were divided to the area of electrode obtaining values of current density.

Current density (J) is defined as the electric current per unit area of cross section. It is defined as a vector whose magnitude is the electric current per cross-sectional area at a given point in space (Lerner and Trigg, 1991). The current density is a figure widely used in electrochemical processes. Figure 16 shows the evolution of current density versus time for the different potential differences considered.

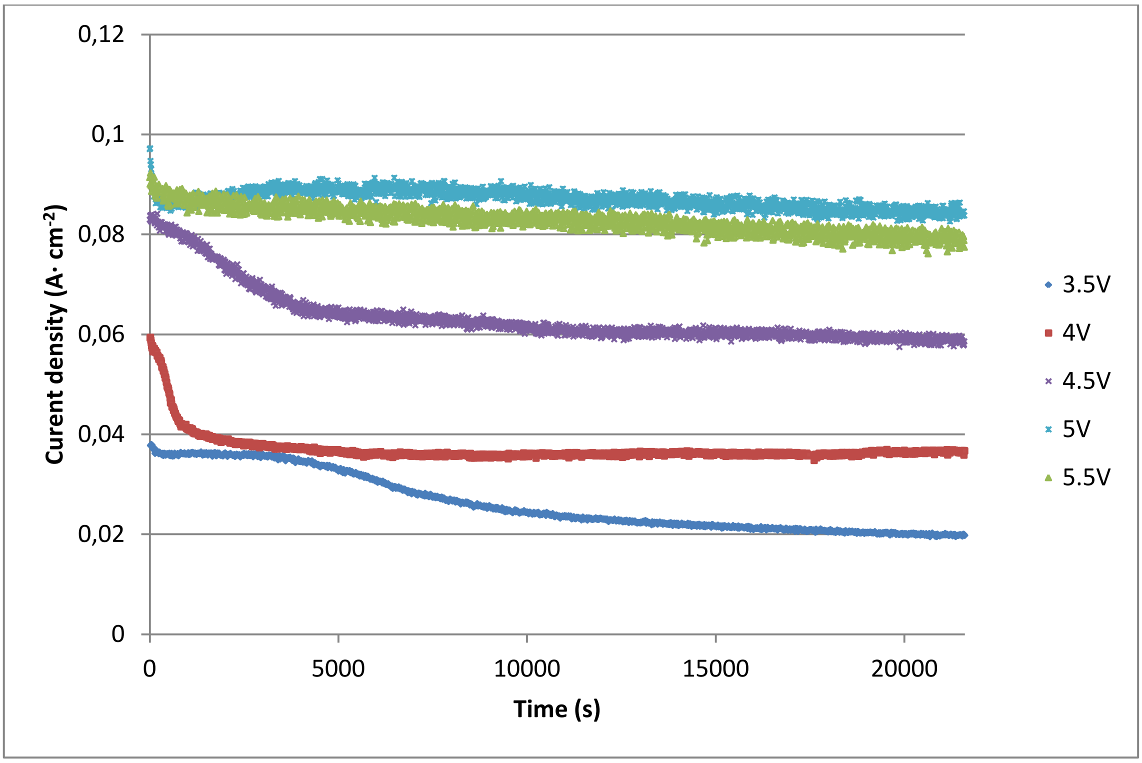

Figure 16. Experimental evolution of current density vs time

The current density data allow us to know the performance of the system. It is expected that increasing the current density higher values of DMC concentration will be obtained, at least in the range of potentials studied. According to these experimental results, applying higher potential values, a higher value of current density is also obtained. For 5.5V, 5V, 4.5V and 3.5V the period considered in the experiments (6h) is not enough to observe a stable value of current density. In the 4V experiment, it seems to be enough time to the current density to be stabilized in a value ($J=0.036\ A\cdot cm^{-2}$). The difference between 3.5V and 4V is much lower than the difference between 4V and 5.5V data. It is also notorious that the 3.5V current density data seem to stabilize very quickly close to 4V, and then from approximately 5000 seconds, experiences again another drop in the current density without stabilization observed. Moreover, the current density for 5V is slightly higher than for 5.5V. This can only be explained by the fact that this type of electrochemical processes are subject to high variability.

There is no great difference between 3.5V and 4V values which agrees with the DMC concentration values obtained. It is then confirmed that the observation of the evolution of the current density prior to analysis of samples is indicative of how much product can be expected to be formed. On the other hand, the small increase observed from 3.5V to 4V in current density is not equivalent to the even smaller increase in the DMC concentration from 3.5V to 4V. Therefore, the current difference is not being employed in the formation of the desired product so an investigation about the reason of why that amount of current is not being used to form DMC could be carried out in future work.

## 4. CONCLUSIONS

In this work a $CO_2$ electro-valorization process for the synthesis of DMC from methanol using ionic liquid [bmim][Br] and $CH_3OK$ has been evaluated. The purpose was to study the influence of the potential on the formation of DMC. The results were analyzed and compared to previous experimental results.

The analysis confirms that the unique compounds which are formed significantly are DMC and DME. DMC is the desired product and DME a by-product. Comparing with other works, it is clear that using undivided cell is favorable for the formation of product DMC at the range of potential studied. The DMC concentration using undivided cell is much higher than the DMC concentration obtained using a cell divided by membranes.

Potential difference is an operational variable to keep in mind to optimize the formation of DMC. The experimental results are clear about this. In the 5.5V experiment the slope in the evolution of $C_{DMC}$ vs time was higher than in the rest of the experiments, meaning that the rate of DMC formation was higher and so the DMC concentration obtained at six hours. However, there was no great difference between the results at 3.5V and 4V. It may mean that the differences are only visible from higher potential and that for little potentials the difference is too small or even zero regarding to formation of DMC. When changing the potential from 4V to 4.5V there is a great improvement in terms of DMC concentration obtained at 6h.

The influence of the potential on the kinetics of DMC formation is also noticeable. Using higher potential values higher rates of formation are also obtained. The reaction equation for the first six hours reaction can be adjusted to zero-order meaning that the reaction rate is equal to a constant.

The current density obtained for the different experiments indicates that with the increase of the applied potential, higher current density values are also obtained. The analysis of the evolution graph of current versus time may give interesting hints to know if the product is being formed according to the expectations. In the studied cases, there is no substantial difference between the 3.5V and 4V data in terms of

DMC formation what makes suspect that the difference in current density is not being used to form product.

Taking as a starting point the results of this work, new experiments could be conducted to provide additional information about the influence of the potential on the formation of product and by-products after six hours of reaction. Moreover, it could be interesting to focus future work on optimization of operating conditions, electrocatalytic materials and the nature of the reaction medium (e.g, ionic liquids).

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