

Electrosynthesis of dimethyl carbonate from methanol and CO₂ using potassium methoxide and the ionic liquid [bmim][Br] in a filter-press cell: study of the influence of the cell configuration

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Abstract

BACKGROUND: The valorization of CO₂ into added-value products appears as a promising strategy for reducing CO₂ emissions. Dimethyl carbonate (DMC) is an environmentally friendly valuable product, with multiple applications, suggested as a potential gasoline additive. However, DMC has traditionally been produced from hazardous phosgene and CO routes, which encourages the interest in developing new processes. The purpose of this work is to study the influence of the membrane in a filter-press electrochemical cell for the valorization of CO₂ by the electrosynthesis of DMC from methanol in the presence of the ionic liquid [bmim][Br] and CH₃OK and avoiding the addition of carcinogens.

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RESULTS: The performance of the process has been studied using 6 different anion exchange membranes in comparison to undivided configuration and our previous study using a cationic exchange membrane. A significant increase in the initial reaction rate is achieved when no membrane is employed. Regardless which membrane is used, an additional resistance seems to be introduced. A final concentration of $85 \text{ mmol}\cdot\text{L}^{-1}$ was obtained up to 48 h without membrane, which involves a six fold increase regarding our previous work.

CONCLUSIONS: Although better results were obtained when no membrane was used, the study of divided cell has provided experimental evidence that can serve as a reference for the evaluation of future improvements in this electrosynthesis.

Keywords: Carbon dioxide, dimethyl carbonate, methanol, ionic liquid, filter-press cell, membrane

INTRODUCTION

Different strategies for reducing carbon dioxide emissions and mitigating climate change are being developed. Among them, innovative processes for CO_2 valorization that allow converting the CO_2 captured into valuable products have attracted much attention¹⁻⁴.

Dimethyl carbonate (DMC) appears as an environmentally friendly valuable chemical of great interest due to its versatile chemical reactivity and unique physical properties⁵. Its low toxicity and high biodegradability makes it an excellent carbonylating and methylating reagent substituting for strongly toxic phosgene, dimethyl sulfate and methyl iodide (6). DMC is also used as an alkylating agent, as an alternative to conventional solvents and electrolyte solvent for lithium ion batteries^{7,8}. It is an important building block in the production of higher carbonates, carbamates and isocyanates⁹. Moreover, DMC is presented as a potential gasoline additive due to its high oxygen content¹⁰.

DMC has been traditionally produced from the phosgenation of methanol^{9,11}. The high toxicity of phosgene caused the development of the EniChem and UBE processes^{12,13}, based on oxidative carbonylation of methanol and carbonylation of methyl nitrite, respectively. Although both routes avoid use of phosgene, they still need chlorinated derivate catalysts and imply the use of CO hence which the interest in developing new greener and safer processes. Methanolysis of urea, transesterification of ethylene/propylene carbonate and the direct synthesis from CO₂ and methanol are alternative routes being developed^{14,15}. Among these, the direct synthesis of DMC from CO₂ and methanol is suggested as the most promising due to the replacement of toxic raw materials by CO₂ and the substitution of multistep processes by a direct synthesis route which results in waste minimization and high efficiency in terms of the atom economy¹⁶. Furthermore, this interesting route enables the production of DMC and, at the same time, the valorization of CO₂.

However, despite being abundant, nontoxic and inexpensive, CO₂ is characterized by its chemical inertness and high thermodynamic stability. Both chemical and electrochemical methods have been studied for the synthesis of DMC from CO₂ and methanol to overcome this issue. Regarding the chemical path, different catalysts have been considered such as organometallic complexes¹⁷, metal oxides^{18,19}, metal alkoxides²⁰ and Cu-Ni bimetallic catalysts^{21,22}; although high temperatures, typically 100-180°, are required for the reaction⁷. High pressure, up to 20 MPa, or even supercritical conditions to shift the reaction equilibrium have also been studied^{5,23}. Dehydrating agents have also been used to remove the water produced and shift the equilibrium, using two different types of water traps: (i) non-recyclable additives such as orthoesters²⁴ and butylene oxide⁵ and (ii) recyclable agents such as acetals²⁵ or even more attractively molecular sieves^{26,27}, as they do not generate co-

products. However, most of the reported studies using chemical methods for DMC synthesis from CO₂ and methanol generally involve very high conditions of temperature and pressure.

Electrochemical techniques can help to supply the energy needed to valorize CO₂ avoiding these high temperatures and pressures. At the same time, it has been suggested that the electricity required for CO₂ electrochemical valorization processes may be provided by renewable sources, serving as an attractive future way of storing the intermittent and difficult to predict renewable energy as chemical energy^{28,29}. Several published studies report the electrosynthesis of DMC from CO₂ in the presence of ionic liquids (ILs) under mild conditions³⁰⁻³⁸. ILs are salts characterized by negligible vapour pressure, high conductivity and a wide electrochemical window, and have attracted much attention as substitutes for conventional toxic and volatile solvents. However, most of the cited references^{31-34,37} achieved high yields due to the addition as a reaction promoter of methyl iodide, which is a category 2 carcinogen. Others workers avoided the addition of methyl iodide at the expense of using other toxic compounds such as propylene oxide³⁵ or benzyl chloride³⁶. Although all the previous cited works used an undivided electrochemical cell, this type of cell does not allow the study of the development of the process with separated anodic and cathodic compartments. In contrast, divided electrochemical cells are characterised by their wide versatility and easy scale-up, which give them potential for industrial production³⁹. A few references⁴⁰⁻⁴⁴ have employed divided cells in the electrosynthesis of DMC via carbonylation of methanol. However, apart from our previous work⁴⁵, the use of those cells has not yet been studied for the direct electrosynthesis of DMC from methanol and CO₂.

Our group recently studied the feasibility of the direct electrosynthesis of DMC from CO₂ and methanol in bmimBr-CH₃OK media in a filter-press electrochemical cell using a Nafion 117 cation exchange membrane⁴⁵. The evolution of the concentration of DMC up to 48h was

reported and a final concentration of 15.07 mmol L⁻¹ was achieved. The analysis of the by-products obtained in the process was also carried out, with tetramethyl orthocarbonate and dimethoxymethane detected and quantified in the liquid phase. A simplified reaction scheme was also proposed. One of the advantages of this process is that the use of carcinogenic compounds is avoided. Recently extensive research has been carried out on the properties of anion exchange membranes, especially for their use in alkaline fuel cells⁴⁶. However, apart from our previous study, no reports have been found regarding either the use of divided cells or anion exchange membranes for the direct electrosynthesis of DMC from methanol and CO₂.

The aim of this work is to explore the influence of the membrane on the direct electrosynthesis of DMC from methanol and CO₂ in the presence of the ionic liquid [bmim][Br] and CH₃OK in a filter press electrochemical cell. New results using anion exchange membranes are presented and compared to our previous study using a cationic exchange membrane. The performance of the process has also been studied in an undivided configuration and compared to the use of both cationic and anionic membranes. A kinetic analysis of DMC formation operating for up to 48 h is also carried out. This study provides experimental evidence that contributes to developing the available knowledge of this process that can be useful as a reference for the assessment of future improvements.

EXPERIMENTAL

Materials

Methanol (Panreac, PA-ACS-ISO, 99.8%), potassium methoxide (Sigma-Aldrich, 95%), dimethyl carbonate (Sigma-Aldrich, anhydrous, ≥99%), dimethoxymethane (Sigma-Aldrich,

99%), 2-propanol (Sigma-Aldrich, anhydrous, 99.5%) were used as received without further purification. 1-Butyl-3-methylimidazolium bromide [bmim][Br] (IoLiTec, 99%), was dehydrated in an oven at 40° C at total vacuum for 12h since it is highly hygroscopic.

Molecular sieves 3A (Panreac, $\Phi=2$ mm), which have been used as dehydrating agents in other studies on the synthesis of DMC^{26,27} were also dehydrated in an oven at 150° C and atmospheric pressure for at least 24h and then cooled down in a recipient under non-moisture conditions until required. Carbon dioxide (99.7%) was purchased from Air Liquide.

Fumapem® FAA, fumapem® FAA-3, fumasep® FAB-PK-130, fumasep® FAP-450, fumapem® FAAM-40, fumasep® FTAM-A, anion exchange commercial membranes were delivered by FuMA-Tech GmbH and were used as received without further pretreatment.

Experimental set-up

The main elements of the experimental set-up were the same as previously reported⁴⁵ with differences derived from the use of different membranes. The experimental system included two tanks, two peristaltic pumps (Watson Marlow 323 S/D), a potentiostat/galvanostat AutoLab PGSTAT 302 N (Metrohm, Inc.) and a filter-press electrochemical cell (Micro Flow Cell®) supplied by ElectroCell. Two different configurations were used in the electrochemical cell: (i) divided cell in anodic and cathodic compartments by an anion-exchange membrane (Figure 1a) and (ii) undivided cell (Figure 1b).

Pt/Nb plates (99.5% Pt) with a surface area of 10 cm² were used as both cathode and anode. The distance between electrodes was 80 mm for the former configuration (Figure 1a) and 40 mm when no membrane was used (Figure 1b). A leak-free Ag/AgCl 3.4 mol L⁻¹ KCl reference electrode was placed very close to the working electrode surface. The equipment was controlled by General Purpose Electrochemical System (GPES) software.

Electrolyte solutions were heated at 303 K and circulated with a flow rate of 20 ml·min⁻¹. A condensing temperature of 279 K was imposed to minimize methanol losses, using a PolyScience circulating bath (AD07R-20-A12E). A septum device was incorporated in the output of the electrolyte tanks to enable sampling.

Experimental procedure

A similar procedure to our previous work was used in this study⁴⁵. In a typical procedure, each of the tanks was filled with 200 mL of methanol in which 30 g of bmimBr and 11 g of CH₃OK had been added. Then, CO₂ was bubbled into the corresponding tank to the working compartment until saturation. Prior to each experiment, the anion-exchange membranes were stored in methanol for at least 12 h before use. Electrodes were also pretreated with HNO₃ (11%) to remove surface adherences and then rinsed with ultra-pure water. All experiments were conducted at a 1.2 V potential between the working and reference electrodes, which corresponded with an average cell potential of 3.5 V.

A different procedure was followed for the experiments in absence of a membrane. The cell configuration was changed as described above and CO₂ was bubbled in the medium. Samples were analyzed in duplicate. Maximum standard deviations for duplicates were less than 15%.

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 mm x 1.40 mm 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 products in the gas phase were identified by GC-MS using manual injection.

RESULTS AND DISCUSSION

Evolution of DMC formation without membrane

In this case, the configuration of the cell was modified as Figure 1b to evaluate the performance of the process in an undivided configuration. For the reference experiment, CO₂ was bubbled until saturation before the beginning of the experiment. No further CO₂ was bubbled during the reaction time. The reference experiment was carried out applying two different potentials: 3.5 V potential between cathode and anode based on our previous work⁴⁵ and 5.5 V potential between the two electrodes based on the literature studies^{30,35}.

As Figure 2 shows, the concentration achieved applying 5.5 V is twice the production obtained using 3.5 V. Regarding its evolution, the concentration of DMC increases constantly from the beginning of the experiment up to 36h. From this time to the end of the experiment, the slope of the curve decreases slightly. Thus, 48h is not long enough to observe how the reaction ends and the concentration of DMC increases only a 13% in the final hours from 71.74 mmol·L⁻¹ in 36h to 80.85 mmol·L⁻¹ in 48h when 5.5V are applied, and 6.7% from 38.14 mmol L⁻¹ in 36h to 40.68 mmol·L⁻¹ in 48h when 3.5V are applied.

In an attempt to shift the equilibrium of the reaction and improve its production, two studies have been performed: (i) constant bubbling of CO₂ during the experiment and (ii) the use of molecular sieves 3A.

Using constant bubbling of CO₂, an increase in the production was expected. However, only a slight improvement is detected in the first hours compared to the bubbling of CO₂ until saturation (Figure 2). This minor deviation decreases as the reaction occurs. This may be due to the experiments being conducted under atmospheric pressure and no significant

improvements could be achieved at low pressures. This agrees with the results obtained using physical dehydrating agents described below.

Molecular sieves were also tested as dehydrating agents to trap the water being formed and shift the equilibrium to a higher production of DMC ($\text{CH}_3\text{OH} + \text{CO}_2 \rightarrow \text{DMC} + \text{H}_2\text{O}$).

Molecular sieves are crystalline aluminosilicates with a three-dimensional framework structure of SiO_4 and AlO_4 distributed in tetrahedral chains linked through oxygen atoms⁴⁷.

They have a very narrow distribution of micropores and only components with critical diameter smaller than the opening of the micropores will be adsorbed⁴⁸. As the critical molecular diameter for the H_2O molecule is 0.26 nm⁴⁸, 3A molecular sieves were selected. In this work 30 g of molecular sieves 3A were held in the tank using a hand-made mesh and CO_2 was bubbled until saturation, as in the reference experiment.

As in the previous experiment only, an insignificant increase is observed over the first hours compared to the reference experiment. As time goes by, this difference is reduced to almost zero. A remarkable improvement in the productivity was expected based on the work of Choi *et al.*²⁶, who found an approximately 15 times increase in the yield using molecular sieves at 300 bar and 453K. However, such an improvement was not found in our study. Obviously, the conditions differ considerably between both studies. Adsorption is a process well known to be favoured at high pressure and our experiments are carried out under atmospheric pressure. Before use the zeolites were cooled in a recipient under anhydrous conditions and tests were also carried out placing the zeolite immediately in the experimental system to avoid hydration without any appreciable difference in the results. Moreover, we suspect that not only water but also CO_2 is adsorbed on the molecular sieves as the critical diameter of the CO_2 molecule is 0.28 nm (<0.3 nm).

It can also be observed from Figure 2 that the evolution of DMC is very similar in the three experiments. The concentration increases almost linearly with time until 36h. The last 12h this increase is lower and lesser than 15%.

Study with anion-exchange membranes

I. Influence of the type of anion-exchange membrane

In this work, several anion exchange membranes have been tested. Fumapem® FAA (FAA), fumapem® FAA-3 (FAA-3), fumasep® FAB-PK-130 (FAB), fumasep® FAP-450 (FAP), fumapem® FAAM-40 (FAAM), fumasep® FTAM-A (FTAM) were provided by FuMA-Tech GmbH.

The results obtained with the different membranes are summarized in table 1, where the concentration of DMC observed after 24 h is reported. As table 1 shows, the best results were obtained with the FAB membrane, which is a transparent brown membrane with a thickness of 130 μm . The concentration obtained with this membrane was $9.74 \text{ mmol}\cdot\text{L}^{-1}$ in 24 h, while the experiment with FAA-3 was not possible because the membrane immediately dissolved in contact with the medium. FAB and FAA-3 are both based on polyaromatic chemistry with quaternary ammonium groups. However, FAB is much stronger cross-linked with polyether ether ketone (PEEK) reinforcement. Hence, FAA-3 was degraded because of the strong nucleophile attack of potassium methoxide, while FAB presented high chemical and mechanical resistance.

FAA was the second best performing membrane achieving 25% lower concentration compared to FAB, with a $7.29 \text{ mmol}\cdot\text{L}^{-1}$ concentration. This membrane is obtained as a transparent film with a thickness of 40-45 μm and no reinforcement. It is stable in both acidic and alkaline media and is based on polysulfone with quaternary ammonium groups. Although

acceptable results were obtained with FAA, little holes appeared after long periods of operation (longer than 24h). Hence, the polysulfone chemistry appears to be unstable under these conditions and thus appears to be less acceptable than the FAB membrane.

FAP and FTAM provided the worse results, giving respectively 28% and 37% less yield than FAB. The former is a transparent film with no reinforcement and a thickness of 50 μm , described in the technical data sheet as low resistant and highly stable in acidic environment. After operation, the FAP membrane turned from transparent to black. This colour change was also observed before applying the electric current, just a few hours after contact between the membrane and the strong alkaline solution. This phenomenon appears to be produced by a reaction of the matrix polymer and not the active component in the membrane. Thus, the functionality might be preserved even when the colour changed to black. No holes were observed during operation, just the colour change. However, long term operation is not recommended by the suppliers under strong alkaline conditions. A product concentration of 7.01 $\text{mmol}\cdot\text{L}^{-1}$ was observed with this membrane. FTAM was also tested, producing a final product concentration of 6.13 $\text{mmol}\cdot\text{L}^{-1}$. This membrane is characterised by its high thickness (700 μm) and a polyamide reinforcement, which gives the membrane excellent mechanical stability but a thick appearance. Due to this high thickness the exchange rate was really low, which could explain the lower concentration of DMC obtained.

The FAAM membrane presented high resistance to ion exchange as, according to the technical data sheet, it needs highly caustic (6-12 mol L^{-1} KOH) conditions to operate. It is a transparent brown membrane based on a benzimidazole type polymer with a thickness of 40 μm with no reinforcement. Under the conditions of our study, the resistance of the membrane was such that no current flux was observed and so no DMC was formed.

Table 1. Synthesis of DMC using different anion exchange membranes up to 24 h. C_{DMC} represents the concentration of DMC obtained after 24 h of operation.

Anion-exchange membrane	Thickness (μm)	Reinforcement	Chemical structure	C_{DMC} ($\text{mmol}\cdot\text{L}^{-1}$)
FAA	40-45	None	Polysulfone composition	7.29
FAA-3	130	None	Polyaromatic structure with quaternary ammonium groups	-
FAB	130	PEEK	Same as FAA-3 but stronger crosslinking	9.74
FAP	50	None	Partially fluorinated structure with ternary amine groups	7.01
FAAM	40	None	Polyaromatic structure with ternary amine groups	-
FTAM	700	Polyamide	Polystyrene structure with quaternary ammonium groups	6.13

II. Evolution with FAB anion-exchange membrane

The time evolution of the production of DMC up to 48h was studied using the best performing anion exchange membrane (FAB). As Figure 3 shows, the concentration of DMC increases constantly, achieving a maximum concentration of $13.74 \text{ mmol}\cdot\text{L}^{-1}$ at the end of the experiment. The rate of production decreases with time, increasing the concentration only by 12.7% in the final 12h compared to 25% in the 12 previous hours.

Comparison of DMC formation using cationic, anionic and no membrane

First of all, it is interesting to compare the by-products identified in the experiment using undivided configuration and the FAB anion exchange membrane to the by-products obtained in our previous study using a Nafion 117 cation exchange membrane⁴⁵. When the Nafion membrane was used, tetramethyl orthocarbonate (OC) and dimethoxymethane (DMM) were

detected and quantified in the liquid phase, especially during the last hours of the experiments⁴⁵. From the liquid phase analysis of both experiments using the FAB membrane and no membrane, tetramethyl orthocarbonate was not detected and dimethoxymethane was below the limit of quantification unlike the previous work. However, dimethyl ether and bromomethane are again detected absorbed in the liquid phase. From the gas phase analysis of the experiment without a membrane, the formation of dimethyl ether and bromomethane was confirmed.

Regarding the quantification of DMC, Figure 3 shows its evolution comparing the results of the three previously studies described using cation and anion exchange membranes and no membrane. As can be seen the concentration of DMC follows a different behaviour with time for the different experiments. When FAB and Nafion 117 are compared, it should be noted that a similar concentration, approximately $15 \text{ mmol}\cdot\text{L}^{-1}$, is achieved after 48 h. Using the FAB membrane the concentration of DMC does not increase strongly during the first hours as happened with the Nafion membrane, but it increased slowly and progressively throughout the experiment. While when the Nafion membrane was used the concentration of DMC no longer increased after 12 h, when the cell is divided with the FAB membrane 48h was not long enough to observe how the maximum concentration of DMC is reached. The fact that the maximum concentration is achieved with a higher rate for the Nafion membrane, could be related to the detection of by-products in the liquid phase after 12 h. Those by-products would be formed from further degradation of DMC once the maximum concentration is reached (longer than 12h), as proposed in the previous reaction scheme⁴⁵. That could be the reason why no liquid by-products are detected up to 48h in the FAB experiment, as the maximum concentration has not yet been reached. The cationic or anionic character of the membrane separating both compartments does not seem to have any influence in the final concentration. Regardless of what membrane is used, an additional resistance seems to be

introduced. That would explain the fact that a higher productivity was obtained when the compartments were not divided. Among both the membranes studied, such resistance would be higher for the FAB membrane, as it takes a longer to reach the same production level and a delay is observed in the appearance of by-products.

Kinetic analysis of DMC formation

Based on the results presented in the previous subsections, the kinetic analyses of DMC formation using the FAB membrane and in absence of membrane were performed following the differential method. Consequently, the experimental data of the evolution of the DMC concentration up to 48 h were fitted and the corresponding rates of DMC formation were calculated as described by Eq. 1:

$$r_{\text{DMC}} = \frac{1}{A} \frac{dn_{\text{DMC}}}{dt} = \frac{V}{A} \frac{dC_{\text{DMC}}}{dt} \quad (1)$$

Where n_{DMC} is the number of moles of DMC formed, V is the volume of electrolyte ($V = 0.2$ L) and A is the electrode area ($A = 10 \text{ cm}^2$).

Figure 4 shows the experimental formation rate of DMC represented vs. the concentration of DMC using the FAB membrane and without a membrane, together with the results obtained in our previous work using Nafion 117⁴⁵. A linear relationship between the formation rate and the concentration of DMC obtained can be seen for the different cases. The maximum DMC formation rate is achieved initially, and then the rate decreases linearly as the concentration of DMC increases. The maximum value for the concentration of DMC can be obtained from the intersection between the curve and the horizontal axis. Hence, it can be observed (Figure 4) that after 48 h operation the maximum concentration of DMC in the experiment without a membrane has not yet been achieved, as the curve does not reach the horizontal axis.

The experimental behaviour can be described by Eq. 2:

$$r_{\text{DMC}} = k_0 - k_1 \cdot C_{\text{DMC}} \quad (2)$$

Table 2 shows the corresponding coefficients calculated with 95% confidence limits compared to those obtained in the Nafion study.

Table 2. Kinetic coefficients obtained for the Nafion 117⁴⁴, FAB and no membrane experiments.

	k_0 (mmol·m ⁻² ·h ⁻¹)	k_1 (L·m ⁻² ·h ⁻¹)	R^2
Nafion 117	587.2 ± 57	38.96 ± 4.66	0.952
FAB	154.8 ± 6.3	10.71 ± 0.77	0.995
No membrane	853.0 ± 43	10.00 ± 0.91	0.992

The values of the coefficients for the three different cases vary, but the meaning can be considered quite similar. The existence of a first constant term describing the formation of DMC is suggested (k_0). As the reagent methanol is in excess, a zero order is observed. As can be seen in Figure 4 and Table 2, a threefold decrease in the initial formation rate of DMC using the FAB anion exchange membrane ($k_0=154.8$ mmol·m⁻²·h⁻¹) is observed in comparison to the Nafion 117 membrane ($k_0=587.2$ mmol·m⁻²·h⁻¹), while a significant increase of around 45% in the initial formation rate is seen when no membrane is used ($k_0=853.0$ mmol·m⁻²·h⁻¹).

The second term represents the degradation rate of DMC due to secondary reactions (k_1) and is directly proportional to the observed concentration of DMC. This term is insignificant in the first hours of reaction, as no DMC is produced. This explains the highest value of the formation rate achieved initially. This coefficient has a similar value for the experiments using FAB ($k_1=10.70$ L·m⁻²·h⁻¹) and no membrane ($k_1=10.00$ L·m⁻²·h⁻¹). Thus, a threefold

decrease is again observed in this value compared to our previous work ($k_1=38.96 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ using a Nafion membrane⁴⁵). This is consistent with the fact that neither OC nor DMM are observed as by-products throughout the reaction. Consequently, this degradation rate corresponds mainly to gas by-products such as dimethyl ether, dehydration product of methanol detected in the GC-MS analysis. Moreover, as the reaction occurs the DMC produced increases and the formation rate decreases. It can be concluded from Figure 4 that the formation rates of DMC tend to zero as the concentration of DMC reaches its maximum value. This maximum concentration ($C_{\text{DMC,max}}$) could be calculated by Eq. 3:

$$\frac{k_0}{k_1} = C_{\text{DMC,max}} \quad (3)$$

Where $C_{\text{DMC,max}}$ has values of $14.45 \text{ mmol}\cdot\text{L}^{-1}$ (0.15 wt%) and $85.3 \text{ mmol}\cdot\text{L}^{-1}$ (0.91 wt%) for the FAB membrane and no membrane studies, respectively, based on the corresponding coefficients estimated from Eq. 2. This implies an increase in the yield (based on CO_2) from 11.98% using the FAB membrane to 70.71% with no membrane. The concentration of DMC when FAB is used is clearly similar to the value obtained from the equivalent Nafion model ($15.07 \text{ mmol}\cdot\text{L}^{-1}$)⁴⁵. While the maximum concentration was obtained after almost 12 h reaction for the Nafion membrane, it takes more than 48 h to achieve the same value with the FAB membrane. In contrast, a significant improvement in the process was achieved when no membrane is used, maintaining the lower degradation rate (k_1) of the FAB experiment and increasing the initial reaction rate. Consequently, a six fold increase is obtained in the final concentration of DMC.

CONCLUSIONS

The influence of the membrane in a divided electrochemical cell for the valorization of CO_2 by the electrosynthesis of DMC from methanol in the presence of the ionic liquid [bmim][Br]

and CH₃OK and avoiding the addition of carcinogens has been studied. New results using different anion exchange membranes have been presented and compared to our previous study using a cationic exchange membrane and to the results obtained without a membrane. Regardless of what membrane is used, an additional resistance seems to be introduced.

Constant bubbling of CO₂ and the presence of 3A molecular sieves have also been tested in the attempt to achieve higher productivities of DMC. However, only slight improvements were detected during the first hours.

Based on the results obtained for the most suitable anion exchange membrane operating for up to 48 h (FAB membrane) and the results achieved when no membrane is used, the kinetic analysis of DMC formation is carried out.

A final concentration of 85 mmol·L⁻¹ was obtained up to 48 h without membrane, which indicates a six fold increase over our previous work. Although better results were obtained when this configuration was used, the study of a divided cell has provided experimental evidence that contribute to the development of the knowledge available about the electrosynthesis of DMC from methanol and CO₂ in the presence of CH₃OK.

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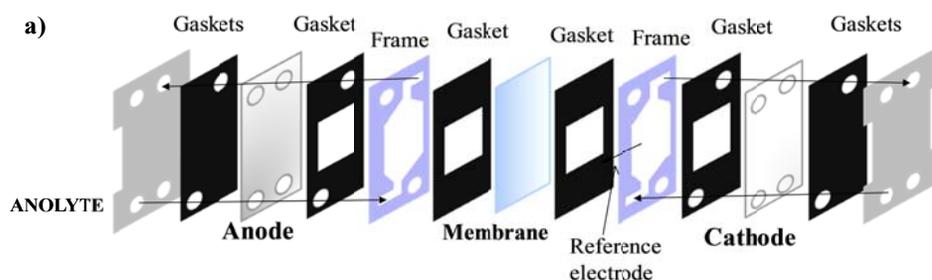
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FIGURES



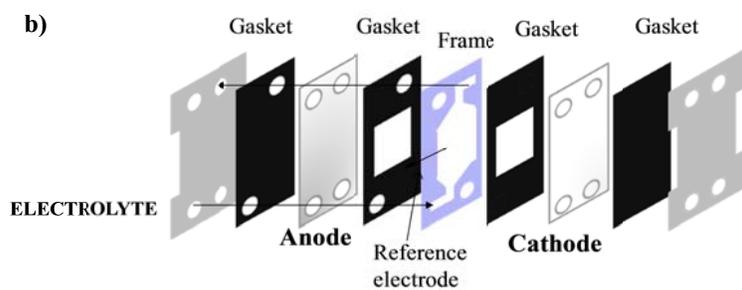


Figure 1. Scheme of the filter-press electrochemical cell in divided configuration (a) and in undivided configuration (b)

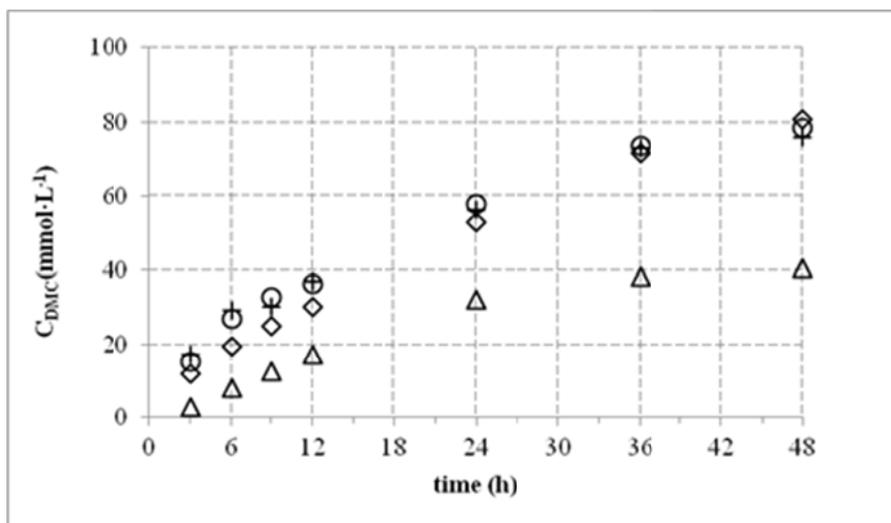


Figure 2. Time evolution of DMC for different experiments: (Δ) 3.5 V CO₂ bubbling upto saturation, 5.5 V CO₂ bubbling upto saturation (◇), 5.5 V CO₂ constant bubbling (○) and 5.5 V molecular sieves (+).

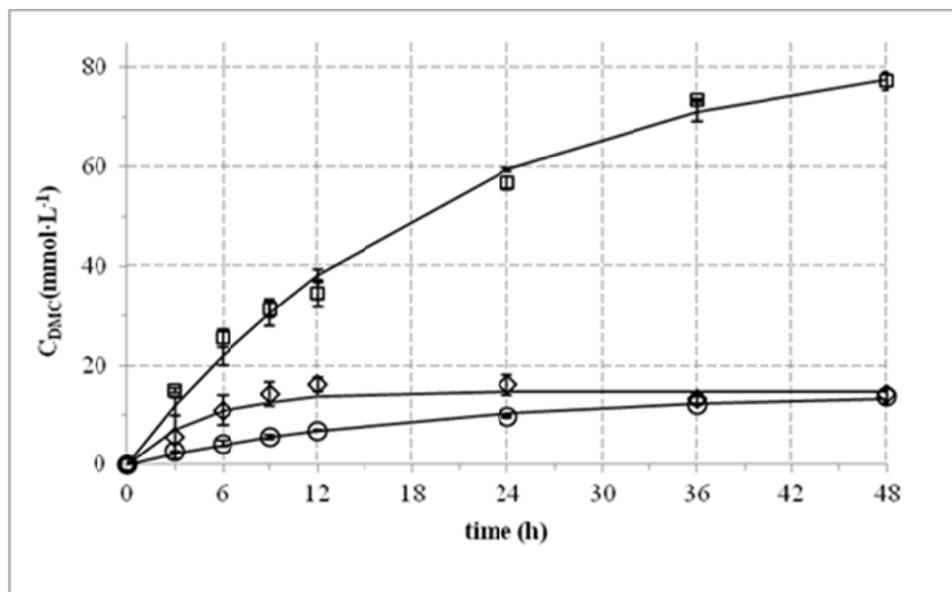


Figure 3. Time evolution of DMC for different experiments: using FAB-PK (○) membrane, using Nafion 117 membrane (◇) and without membrane (□).

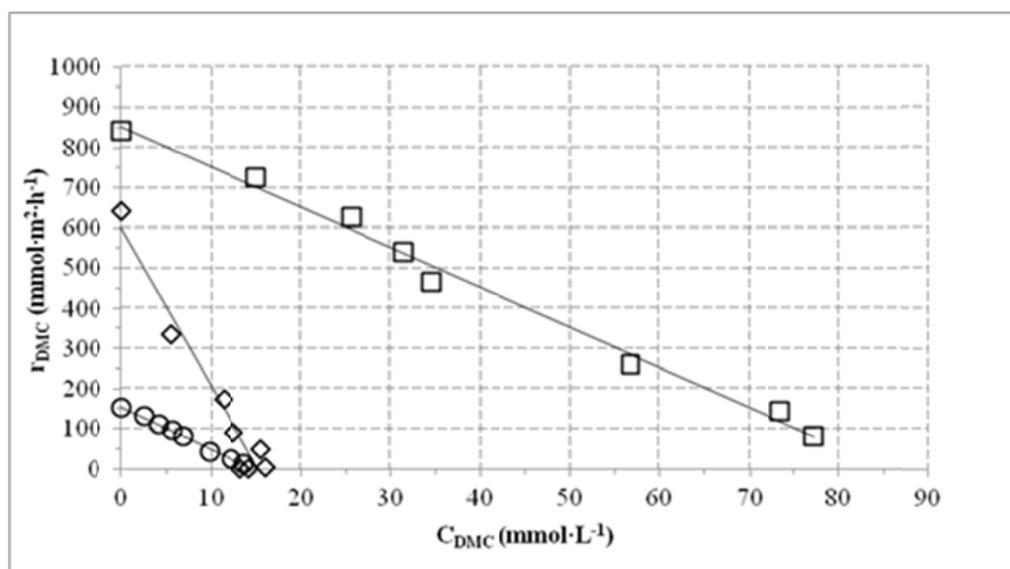


Figure 4. Experimental reaction rates, (r_{DMC}), vs. C_{DMC} of different experiments: reaction rate of DMC using FAB-PK membrane (○), using Nafion 117 membrane (◇) and without membrane (□). (-) Fitting of all the data