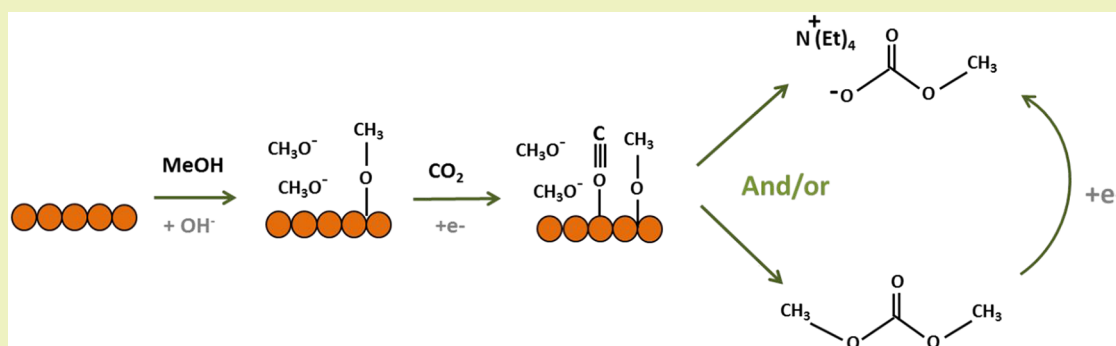# Electrochemical Conversion of $CO_2$ into Organic Carbonates—Products and Intermediates

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S Supporting Information

**ABSTRACT:** In this work, we report a spectro-electrochemical study of the synthesis of organic carbonates from $CO_2$ and methanol. The obtained spectra reveal the presence of a species with vibrational features at 1673 and 1281 $cm^{-1}$ that originate from the reaction of methanol with CO from $CO_2$ electrochemical reduction. Both methanol activation and the formation of CO from $CO_2$ (rather than $CO_2^{•-}$ as considered in previous literature) were necessary conditions for the formation of this product. This species was identified as an alkyl ammonium methyl carbonate and was found on three different electrode materials. Although dimethyl carbonate was not directly identified under the studied conditions, it was observed that it decomposes under an effect of the applied potential to the same alkyl ammonium methyl carbonate. Therefore, although it appears to be possible to synthesize dimethyl carbonate electrochemically from $CO_2$ and methanol, dimethyl carbonate is not stable under the reductive conditions considered.

**KEYWORDS:** electrosynthesis, carbon dioxide, methoxycarbonyl, dimethyl carbonate

## INTRODUCTION

$CO_2$ amounts in the atmosphere are increasing continuously, generating an issue of global concern as $CO_2$ is one of the major contributors to the greenhouse effect.[1] Hence, the study of $CO_2$ conversion has attracted the interest of the scientific community in the last decades, and the development of new technologies for $CO_2$ utilization has become a topic of high societal interest.[2]

Other than being a greenhouse gas, $CO_2$ can also be seen as a cheap source of carbon. It is safe, abundant, renewable, and the technologies for its sequestration are already well established.[3−5] Its conversion into useful and commodity chemicals, as for example organic carbonates,[6−8] will not only contribute to carbon-neutral processes, but it may also have economical and industrial advantages. In the particular case of the use of electrochemical methods for $CO_2$ conversion; the range of advantages is potentially even wider as with electrochemistry; the usage of toxic reactants is reduced; the selectivity of the processes can be tuned; and more importantly, renewable energy sources can be used.[9]

The use of $CO_2$ as a source of carbon for synthesis has a wide range of applicability and can go from the synthesis of hydrocarbons, to alcohols and organic carbonates.[10] However, the development of any of these processes to an industrially applicable technology is still far from reality. Concerning the synthesis of organic carbonates, recent studies[8] have shown that novel electrochemical routes for, for example, dimethyl carbonate (DMC) from $CO_2$ still require significant efforts focused on increasing yields and reducing energy consumption of the process.

The synthesis of DMC from $CO_2$ and methanol has been reported in different nonaqueous solvents such as organic solvents[11−13] and ionic liquids.[14,15] The use of these solvents is related with the solubility of $CO_2$ in nonaqueous systems being higher than in aqueous systems.[16] Moreover, nonaqueous solvents are known for stabilizing $CO_2$ reduction intermediates such as $CO_2^{•-}$, which is often considered as an important intermediate in organic synthesis. In fact, the anion radical has been assumed to be the most important species in the

carboxylation of methanol to produce DMC. However, none of the aforementioned studies report about the electrochemical stability of DMC.

As mentioned, a major issue in the electrochemical synthesis of DMC is the low yield.[8] For example, in the existing publications for this reaction in organic solvents,[11−13] the maximum reported yield is around 30% of methanol conversion.[13] However, this yield is obtained not directly from the electrochemical conversion but only after methylation with methyl iodide.

Another issue is that in the majority of cases, the mechanism reported for the electrosynthesis of DMC (or other carbonates) from $CO_2$ and methanol (or other alcohols) is presented without clear evidence for the intermediates involved. On the other hand, in heterogeneous catalysis, there are papers in which reaction intermediates such as methoxy and methoxycarbonyl species were identified by the use of in situ infrared spectroscopy.[17−19] The lack of similar fundamental information about the electrochemical reaction is clearly a drawback for the development of more efficient, selective, and sustainable synthesis processes.

In this work, we report for the first time the use of spectro-electrochemical methods to shed light onto the reaction mechanism and the corresponding intermediates involved in the synthesis of DMC from methanol and $CO_2$. Our results show the formation of an intermediate containing C=O and C−O groups from the reaction between methoxy groups from methanol with electrochemically generated CO from $CO_2$ electroreduction. The formation of this alkyl carbonyl intermediate is observed on different electrode materials (Cu, Pt, and Pb) as well as for other alcohol substrates (ethanol). In gas-phase reactions, this species has been identified as a methoxycarbonyl intermediate, but our results demonstrate that under electrochemical conditions, it corresponds to an alkyl ammonium monomethyl carbonate. DMC was not directly observed by FTIR because it was shown to suffer from decomposition due to the negative potential into the monomethyl carbonate (the only detectable product from reaction between $CO_2$ and methanol). The fundamental understanding of the reaction mechanism provided by this study is a step further in the achievement of electrochemical methodologies for the synthesis of organic carbonates from $CO_2$.

## ■ EXPERIMENTAL DETAILS

The voltammetric experiments were performed in a three-electrode cell at room temperature using a Pt coil as counter electrode and an Ag/Ag$^+$ reference electrode. This reference electrode was prepared with an Ag wire in a solution of 0.1 M AgClO$_4$. This reference electrode was prepared with an Ag wire in a solution of 0.1 M AgClO$_4$ (97% from Aldrich) in acetonitrile (MeCN, 99.8% anhydrous from Sigma-Aldrich) as described previously.[20] The working electrodes (Cu, Pt, and Pb discs) were polished with alumina suspension, rinsed with Milli-Q water (18.4 MΩ) and sonicated for 5 min before each experiment. The electrode potential was controlled with a Potentiostat 466 System (Model ER466) from E-DAQ. The acetonitrile solutions containing 0.1 M of supporting electrolyte (tetraethylammonium tetrafluoroborate ≥99% from Fluka − TEABF$_4$,) were purged with Ar (6.0, Linde) during 10 min prior to the experiments to remove oxygen. Before the measurements, the solution was saturated with $CO_2$ (4.5, Linde) by bubbling the gas for 20 min in the solution and

methanol (or ethanol, both anhydrous 99.8%, Sigma-Aldrich) was added in a concentration of 10 or 100 mM. During the electrochemical/spectroelectrochemical measurements, the gas flow was kept in the cell atmosphere. All the chemicals were used without further purification, and for this reason, it should be kept in mind that solutions contain residual amounts of water (∼40 ppm).[20]

In situ Fourier transform infrared (FTIR) spectroscopy (Bruker Vertex 80 V IR spectrophotometer) was used to characterize the products and intermediates of the reaction. A CaF$_2$ prism bevelled at 60° was used and the spectra correspond to an average of 100 interferograms with 8 cm$^{-1}$ resolution and p-polarized light.

The spectra were obtained in a thin layer configuration where the electrode is pressed against the prismatic window at controlled potential of −1.0 V (vs the Ag reference). At this potential (where no Faradaic process was detected), a spectrum was obtained which was used as background. Next, the electrode potential is changed, and the sample spectrum is obtained. After normalization with the background spectrum (to remove solvent and other spectral interferences), the final spectra are presented as absorbance spectra, according to $A = -\log(R/R_0)$ where $R$ and $R_0$ are the reflectance corresponding to the single beam spectra obtained at the sample and reference potentials, respectively. In these difference spectra, negative bands (pointing down) correspond to species that were present on the electrode at the reference potential and that have been "consumed" at the sample potential, and positive bands (pointing up) correspond to the formation of species at the sample potential. All the spectro-electrochemical experiments were performed at room temperature, with an Ag/AgClO$_4$ and a platinum coil used as reference and counter electrodes, respectively.

The transmission spectra from the solution species spectra were collected using a SeZn window with an incident angle of 60° and obtained by averaging 100 scans with a resolution of 8 cm$^{-1}$. It is important to mention that FTIR experiments in the thin-layer configuration used here are not suitable for a quantitative evaluation of product yields or Faradaic efficiencies. Our experiments focused on identifying intermediates and gaining mechanistic insights.

## ■ RESULTS AND DISCUSSION

**Electroreduction of $CO_2$ and MeOH.** The voltammetric curve for the combined electroreduction of $CO_2$ and MeOH on a Cu disc electrode in 0.1 M TEABF4 in MeCN is compared with the CVs for the separate compounds in Figure 1.

The blank CV shows a wide potential window for Cu in acetonitrile, limited at negative potentials by the reduction of residual water in the electrolyte and at positive potentials by the decomposition of MeCN.[20] As previously reported,[20] in the presence of $CO_2$, reductive currents start to be observed at −1.6 V, corresponding to its reduction to CO and conversion to (bi)carbonates, respectively. When 10 mM of MeOH is added to the solution, two new features can be observed in the cathodic sweep (at −1.63 and −1.88 V), most likely corresponding to the formation of adsorbed species (methoxy groups as confirmed below with the FTIR results). Moreover, at more negative potentials, an increase in the reduction current around −2.3 V is also observed. This reduction current can be due to MeOH reduction to $CH_4$ or to water reduction, the content of which will be higher when MeOH is added to
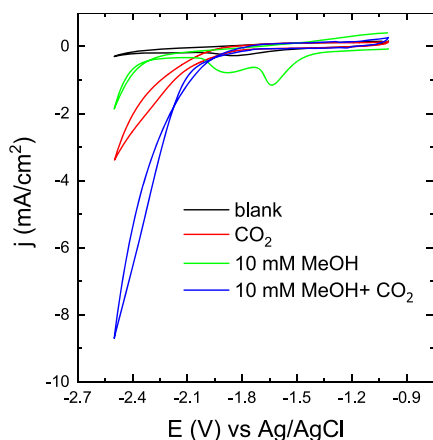
**Figure 1.** CVs obtained at 100 mV/s in 0.1 M TEABF$_4$ in MeCN with a Cu electrode under Ar atmosphere (black line), under CO$_2$ atmosphere (red line), with 10 mM MeOH (green line) and with 10 mM MeOH with CO$_2$ atmosphere (blue line).

the electrochemical cell, even though anhydrous MeOH (~0.01% water content) was used in the experiments.

Interestingly, in the presence of CO$_2$ (blue line, Figure 1), the first two peaks observed for MeOH are absent, and significant reduction currents are observed at potentials more negative than −1.6 V, as also observed for CO$_2$ electrochemical reduction at Cu electrodes in this solvent in the absence of methanol.[20]

The infrared spectra presented in Figure 2 were obtained at different electrode potentials for 0.1 M MeOH in 0.1 M
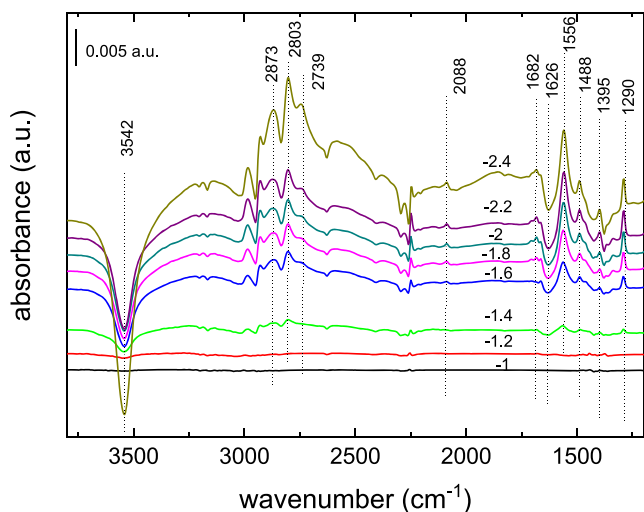


**Figure 2.** FTIR spectra for 0.1 M TEABF$_4$ in MeCN with 10 mM of MeOH at a Cu electrode at different electrode potentials between −1.2 and −2.4 V with reference spectrum at −1.0 V.

TEABF$_4$ in MeCN. The results show vibrational bands related not only with MeOH but also with MeCN and the supporting electrolyte. At 3542 and 1626 cm$^{-1}$, the OH stretching and OH bending, respectively, from both MeOH and residual water are observed. In the region of 2300 cm$^{-1}$, the characteristic bands for the CN groups from MeCN are observed. These bands are due to CN involved in solvation shells (interacting with BF$_4$ groups) and CN free from solvation.[20] In the lower frequency region, between 1700 and

1250 cm$^{-1}$, the spectra present several bands, mostly related with the presence of TEA$^+$ cations near the electrode surface and also with decomposition products from MeCN (i.e., acetamides). In the wavenumber region from 2880 to 2700 cm$^{-1}$, bands due to the CH$_3$ stretching groups from MeOH are observed.[19] These bands are not observed in the absence of MeOH, and they are observed in the spectra for potentials more negative than −1.2 V, at the same potentials for which in the CV for solutions with 0.1 M MeOH the first voltammetric feature appears. It is worthwhile to mention that molecular methanol C−H vibration modes are observed at 2940 and 2825 cm$^{-1}$ according with the transmission spectra (results not shown), and for this reason, we attribute the C−H modes at 2873, 2803, and 2739 cm$^{-1}$ to methoxy, as also reported previously in gas-phase experiments.[19] These observations suggest that methoxy groups are formed at or near the electrode surface by dehydrogenation/deprotonation of MeOH, when negative potentials are applied. However, it is important to notice that the deprotonation may also take place by the increasing amount of OH$^-$ formed at these potentials because of the reduction of residual amounts of water. The methoxy groups are considered to be important precursors for the formation of DMC.[18]

In order to identify the species involved in the simultaneous reduction of methanol and CO$_2$, FTIR experiments in MeCN with 10 mM of MeOH and CO$_2$ atmosphere were performed. Figure 3 shows the spectra at different electrode potentials between −1.2 and −2.4 V (A), the transmission spectra for the species in solution (B), and an inset for a smaller potential range (C) under the same conditions as in (A).

In the presence of MeOH and CO$_2$, the results show that when the electrode potential is made more negative, two positive bands at 1674 (due to a C=O group) and 1283 cm$^{-1}$ (due to a C−O vibration) can be observed (Figure 3A). When the electrode potential reaches −1.8 V, CO$_2$ conversion to (bi)carbonates takes place as observed from the positive bands at 1608 cm$^{-1}$ corresponding to the C=O stretching from HCO$_3$$^-$.[20] A closer look at the results at lower potentials (Figure 3 C) shows that the formation of the product/adsorbate occurs already at −1.2 V and, contrary to what is observed without MeOH,[20] the CO$_2$ consumption (negative band at 2300 cm$^{-1}$) also starts at these potentials (~−1.2 V). These observations suggests that the two positive bands at 1673 and 1281 cm$^{-1}$ are related with the reduction of CO$_2$ in the presence of methanol. However, they cannot be attributed to the formation of DMC, as indicated by the transmission spectra in Figure 3B which shows that DMC presents clear IR bands at 1756, 1455, and 1283 cm$^{-1}$. As (bi)carbonates have been previously identified as products of CO$_2$ conversion on Cu electrodes in MeCN,[20] their transmission spectra are also presented in Figure 3B, showing that also (bi)carbonates can be clearly distinguished by FTIR. The bands at 1673 and 1281 cm$^{-1}$ do not correspond with those expected from DMC as shown in Figure 3C, but the results suggest that they are related with the presence of both CO$_2$ and MeOH. These bands have been previously observed in the gas-phase reaction of CO$_2$ and methanol and were attributed to the C=O and C−OCH$_3$ stretching vibrations, respectively.[21]

To clarify if the formation of these intermediates/products is related with the electrochemical conditions or can be formed just by chemical interaction of the species in solution, a series of transmission spectra for solutions with different composition were obtained (Figure S1 in the Supporting Information). The
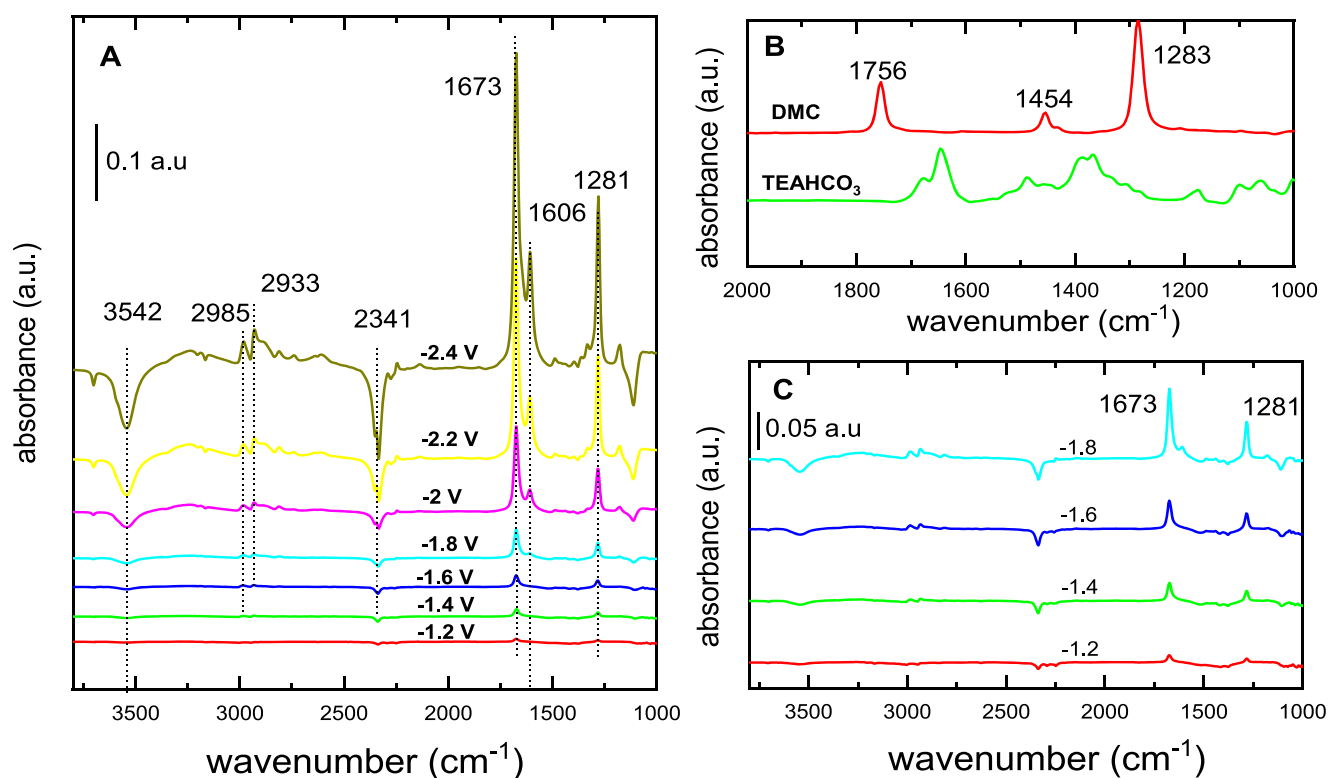
**Figure 3.** FTIR spectra for 0.1 M TEABF4 in MeCN with 10 mM of MeOH and $CO_2$ at a Cu electrode: (A) at different electrode potentials between −1.2 and −2.4 V with reference spectrum at −1.0 V; (B) the transmission spectra for the species in solution of 0.1 M TEABF4 in MeCN (with the electrolyte spectrum subtracted as background) and (C) detailed spectra from −1.2 to −1.8.

results show that independent of the presence of methanol, carbonates, or $CO_2$ in the MeCN solution, the DMC vibrational spectra are not affected, and the bands observed in Figure 3 are due to an electrochemical reaction between MeOH and $CO_2$ or their electrochemical products.

**Isotopically Labeled Compounds.** To provide more details on the nature of the species responsible for the vibrational bands observed in the spectra at 1673 and 1281 $cm^{-1}$, experiments with isotopically labeled compounds were performed. Both $CD_3OD$ and $^{13}CO_2$ were used to ensure the contribution of the two compounds in the formation of the intermediate/product. The obtained results are presented in Figure 4.

For the labeled $CO_2$, the spectra in Figure 4A show a blue shift of the bands related to C=O (from 1673 to 1624 $cm^{-1}$) and C−O (from 1281 to 1266 $cm^{-1}$), as expected from the replacement of the $^{12}C$ by $^{13}C$, suggesting that $CO_2$ or one of $CO_2$ reduction products is responsible for the carboxylation of the methoxy groups from MeOH. In the presence of deuterated methanol, the bands corresponding to intermediate/product are also observed to shift (Figure 4B). For the band at higher wavenumbers (1671 $cm^{-1}$), only a small influence of the deuterium atoms is observed because this band corresponds to a C=O bond that is not directly bonded to any C−D group. However, the C−OCH$_3$ band shifts to higher wavenumbers upon deuteration.

**Effect of the Electrode Material.** The formation of the intermediate/product was tested on other electrode materials, Pt and Pb. These materials were chosen because of their significantly different properties for $CO_2$ electrochemical reduction in organic solvents.[22,23] The spectra obtained for
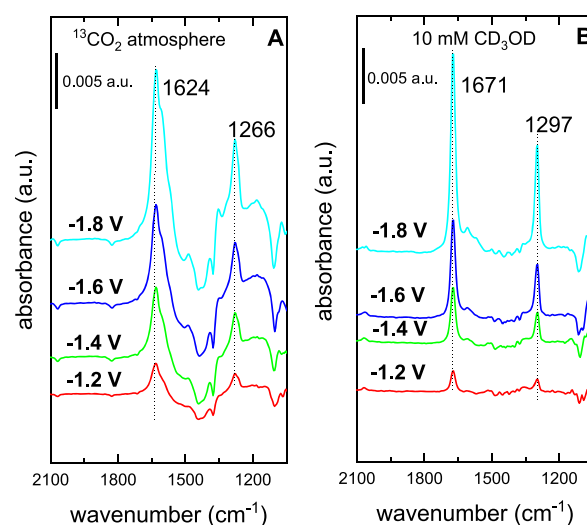


**Figure 4.** FTIR spectra for negative potentials of the Cu electrode in 0.1 M TEABF$_4$ in MeCN with (A) 10 mM MeOH with $^{13}CO_2$ atmosphere and (B) 10 mM $CD_3OD$ saturated with $CO_2$. Background obtained at −1.0 V.

these two electrode materials at different electrode potentials are shown in Figure 5.

Similarly to what is observed for Cu electrodes, the spectra for both Pt and Pb show two well-defined FTIR bands at ca. 1673−1675 and 1281 $cm^{-1}$ from not too negative potentials (−1.2 V). Because of the very similar wavenumbers, these bands can be attributed to the formation of the same intermediate/product as observed for Cu electrodes (Figure 3). Also for Pt and Pb, bands for DMC could not be observed
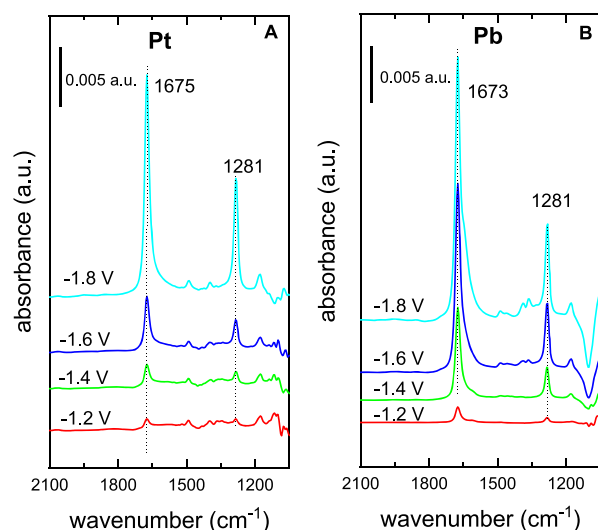
**Figure 5.** Spectra obtained at different electrode potentials for $CO_2$ reduction in 0.1 M TEABF$_4$ in MeCN with 10 mM of MeOH at Pt and Pb electrodes. Background spectra obtained at −0.5 and −1.0 V for Pt and Pb, respectively.
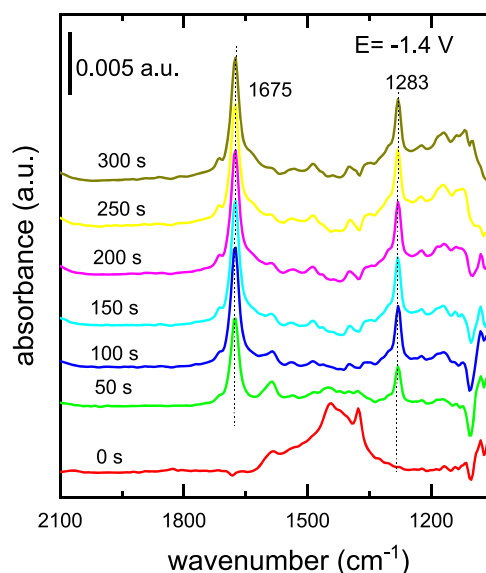


**Figure 6.** Spectra obtained at −1.4 V for the Cu electrode in 0.1 m TEABF$_4$ in MeCN with 10 mM of MeOH at every 50 s during a 300 s period, while purging CO. Background spectrum was taken before starting to purge CO into the spectroelectrochemical cell.

in the spectra. The results show that the product of the electrochemical reaction that is taking place is not dependent on the electrode material and that the carbonylation of the methoxy groups from methanol must be performed by a common reduced form of $CO_2$ (CO or $CO_2^{•−}$) on all three materials studied.

**Formation of Methoxycarbonyl Species from CO and MeOH.** The formation of the methoxycarbonyl intermediate from MeOH and $CO_2$ has been observed previously in heterogeneous catalysts processes (gas phase reactions) for the synthesis of DMC.[19,21,24] However, in some of these reports, this intermediate is obtained under oxidative conditions[19] and in the presence of CO, not $CO_2$. Also, in previous reports, it was shown that CO is a product from $CO_2$ reduction at metallic electrodes in organic solvents.[20,22,25,26] In order to understand which reduced form of $CO_2$ (CO or $CO_2^{•−}$) is the responsible species for the electrocarbonylation reaction, experiments using CO were performed. The spectra were obtained with the electrode at −1.4 V for different times, while CO was bubbled into the solution, and are presented in Figure 6.

In Figure 6, it is possible to observe that the first spectrum (t = 0 s) only presents bands for CH bending (1600−1300 cm$^{-1}$) groups of TEA$^+$ and MeCN. This positive band reflects the attraction of the positive charges into the thin layer at negative electrode potential (−1.4 V). At 50 s, some CO has reached the surface, and bands at 1674 and at ∼1280 cm$^{-1}$ are observed, similarly to the results obtained with $CO_2$ in solution. These results suggest that reaction of the methoxy groups, originated from MeOH, with the CO formed from $CO_2$ reduction is taking place. We emphasize that the application of a potential is still required to provide methoxy groups for carbonylation.

**Identification of the Reaction Intermediate.** The FTIR bands at 1673 and 1281 cm$^{-1}$ as observed for the reaction between MeOH and $CO_2$ have previously been described in the heterogeneous catalysis literature for the CC bond scission of methyl pyruvate over Ni(111) surfaces at 1677 and 1253 cm$^{-1}$, and for MeOH carbonylation with CO on Au(111) at 1655 cm$^{-1}$.[24] In both reports, the authors assign these bands to

the formation of a methoxycarbonyl species (Figure 7A), an intermediate in the formation of DMC. As mentioned above,
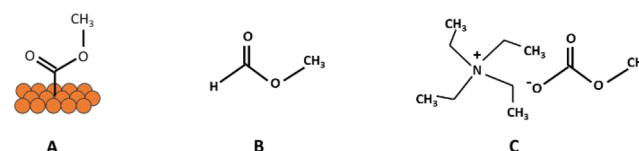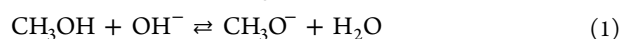


**Figure 7.** (A) Methoxycarbonyl group, (B) methyl formate, and (C) tetraethylammonium methyl carbonate.

MeOH decomposes by the action of the applied potential on the electrode generating methoxy groups. In the presence of CO, carbonylation of the methoxy groups can take place, and a methoxycarbonyl species (or a compound containing a methoxycarbonyl groups) can be formed.

However, the results obtained from FTIR described here show no evidence for an adsorbed intermediate. The stretching frequencies for both the C═O and C−O bands do not show any Stark effect (i.e., a shift of the vibration frequency with the applied potential which is normally considered as a characteristic of adsorbed species) and are the same (within experimental error) for the different electrode materials (the vibration frequency of an adsorbed species should be dependent on the metal onto which it adsorbs).

The methoxycarbonyl structure is very similar to a deprotonated methyl formate (MF) (see Figure 7). MF can be obtained from MeOH carbonylation with CO, in a base-catalyzed reaction according to the reactions:[27]

$$CH_3OH + OH^- \rightleftarrows CH_3O^- + H_2O \tag{1}$$

$$CH_3O^- + CO \rightleftarrows CH_3OCO^- \tag{2}$$

$$CH_3OCO^- + H_2O \rightleftarrows CH_3OCOH + OH^- \tag{3}$$

As the experiments were performed under non dry conditions and water reduction takes place, forming OH$^-$, these reactions could also take place in the vicinity of the

electrode. To evaluate the possibility of the intermediate being deprotonated MF, transmission spectra of this compound with different concentrations of TEAOH (increased pH) were obtained (Figure S3, Supporting Information).

The results show that in pure MeCN, MF presents three bands at 1730, 1213, and 1159 cm$^{-1}$. When increasing the quantities of TEAOH added to the solution, other bands appear in the spectra at approximately 1600, 1380, and 1349 cm$^{-1}$. Simultaneously, the bands observed in pure MeCN decrease in intensity. These results show that the vibrational frequencies for MF and its deprotonated form are different, but none of them matches the vibrational frequencies for the species observed during $CO_2$ electroreduction in the presence of methanol.

It should be mentioned that, in order to rule out any other possible reaction product/intermediate containing C=O and C−O bonds, transmission spectra were measured of formic acid and acetic acid in MeCN and in highly alkaline solutions, MeCN with TEAOH (Figure S2, Supporting Information). The results showed that none of the forms of acetic or formic acid (protonated and deprotonated by strong alkaline media) have FTIR bands corresponding with those observed in the presence of methanol and $CO_2$ (1670/1283 cm$^{-1}$).

**Electrochemical Reduction of DMC in MeCN.** Although the formation of DMC from MeOH and $CO_2$ has been reported previously,[11−13] it could not be confirmed by FTIR under the experimental conditions used in this work. In order to evaluate the electrochemical behavior of DMC under reductive conditions, 10 mM solutions of DMC in 0.1 M TEABF$_4$ in MeCN were studied at Cu electrodes by both cyclic voltammetry and FTIR (Figure 8).
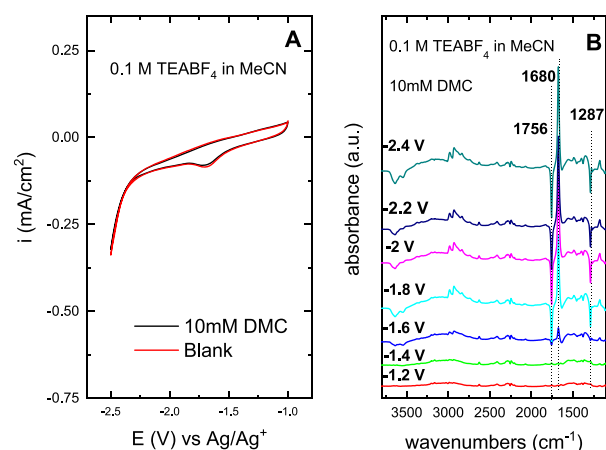


**Figure 8.** Electrochemical behavior of DMC at Cu electrodes in 10 mM DMC solutions in 0.1 M TEABF$_4$ in MeCN: (A) cyclic voltammetry at 100 mV/s; (B) Spectra at different electrode potentials, background spectrum obtained at −1.0 V.

The results show that the cyclic voltammogram remains essentially unchanged in the presence of DMC, suggesting the absence of faradaic processes taking place in this potential window (Figure 8A). However, the FTIR spectra show some interesting features (Figure 8B). The initial bands for DMC (at 1756 and 1287 cm$^{-1}$) become negative at potentials below −1.6 V, where a peak can be observed in the voltammetry (Figure 8A). At this same potential, a new band at 1680 cm$^{-1}$ can be observed (Figure 8B). This result suggests that the

negative electrode potential induces the decomposition of DMC.

It is important to mention that the decomposition of DMC due to changes on the local pH (increasing of OH$^-$ amounts due to water reduction) was also evaluated by taking transmission spectra of DMC at high solution pH, and decomposition was not observed (results not shown).

It has been reported,[28] that DMC decomposition at negative potential can take place. DMC is frequently used as a solvent for lithium ion batteries, and it was observed that its irreversible reduction to lithium methyl carbonate and methane can occur under operating conditions. In order to evaluate the possible reduction of DMC to methyl carbonate (in the present case tetraethylammonium methyl carbonate, Figure 7C), its transmission spectra in acetonitrile was obtained, and the results are plotted in Figure 9.
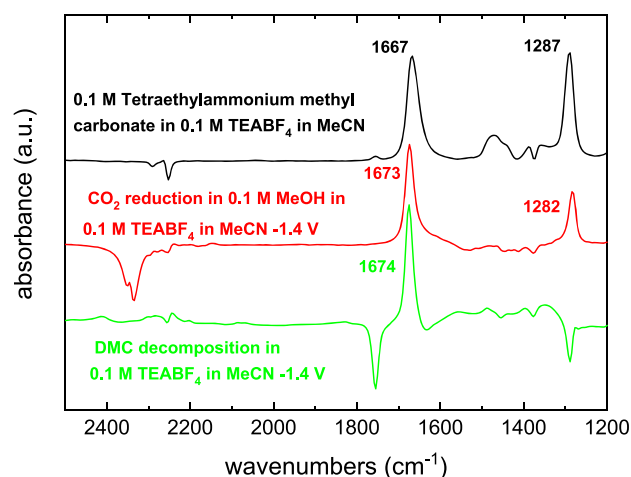


**Figure 9.** Transmission spectra for tetraethylammonium methyl carbonate in 0.1 M TEABF$_4$ in MeCN; background spectrum was obtained with 0.1 M TEABF$_4$ in MeCN. Also presented are the spectra under controlled potential for $CO_2$ reduction with 0.1 M MeOH and DMC decomposition, both at −1.4 V.

The results show that the tetraethylammonium methyl carbonate presents two intense FTIR bands at 1667 and 1287 cm$^{-1}$ corresponding to a C=O and a C−O bond, respectively. These bands are at the same wavenumbers as those observed for both DMC decomposition and electrochemical reduction of $CO_2$ in the presence of MeOH. Small differences in the precise wavenumbers can be due to either experimental error (8 cm$^{-1}$) or to the fact that the cation is slightly different for the transmission spectra and for the electrochemical experiments.

With these results, it can be suggested that the species giving rise to the FTIR bands at ~1670 cm$^{-1}$ and at ~1280 cm$^{-1}$ (C−O) is a methyl carbonate. As shown above, DMC decomposition occurs at negative potentials (below −1.4 V) leading to the methyl carbonate of the respective alkylammonium salt (from supporting electrolyte). These results also explain why DMC could not be found in our experiments on the carboxylation of methanol with $CO_2$. It cannot be confirmed if DMC is also obtained as a product (also because the methane that is the coproduct of the reaction cannot be identified by FTIR), but it is reduced in the same potential range into the mono-methyl compound.

From these results, we suggest that the reaction mechanism (Figure 10) involves the electrochemical reduction of $CO_2$ to
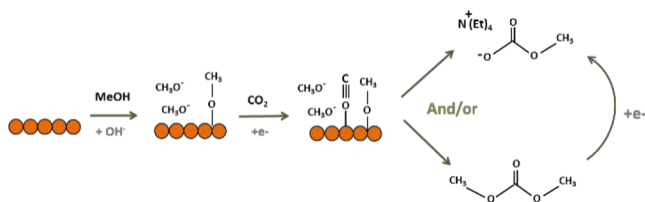


**Figure 10.** Scheme of the proposed reaction cycle.

CO (that was observed for all materials, Figure S5, Supporting Information, though with different rates). At the same time, methanol activation takes places by dehydrogenation/deprotonation by $OH^-$ species coming from the oxidation of residual water, forming methoxy groups on or near the electrode surface. When CO and methoxy are both available, they react to form DMC and/or mono methyl carbonate. If DMC is formed, it is quickly decomposed to the monomethylcarbonate at the relevant electrode potential.

## CONCLUSIONS

In this manuscript, the electrochemical conversion of $CO_2$ with methanol to dimethyl carbonate was studied by using *in situ* FTIR. For the first time, FTIR was applied unravel the details of this electrosynthesis reaction.

The results show that under the electrochemical conditions used in this study, the product of the simultaneous reduction of $CO_2$ and MeOH is the monomethyl carbonate complexed with the cation of the electrolyte (tetraethylammonium). This product forms from the reaction between $CO_2$ and MeOH as revealed by the experiments with the isotopically labeled compounds. Moreover, in contrast to what has been reported previously[12,13] for the electrosynthesis of organic carbonates from $CO_2$, we observed that the reduced form of $CO_2$ responsible for the carboxylation step is CO and not the anion radical. Moreover, the reaction was shown to occur on three very different electrode materials, suggesting that the most important requirements are the formation of methoxy groups from MeOH and the ability of the electrode to reduce $CO_2$ into CO. Similar results have been obtained when another alcoholic substrate, such as EtOH, is used for electro-carbonylation.

Although the direct identification of DMC could not be proven with the FTIR, the results suggest that this product can be formed under the conditions used. However, because of the reducing conditions, DMC decomposes into the corresponding alkylammonium methyl carbonate. Therefore, tetraethylammonium methyl carbonate is considered as the main reaction product of the reaction under the experimental conditions used.

These results represent an important fundamental insight for the understanding of the reaction of $CO_2$ with alcohols under electrochemical conditions aiming at the development of new synthetic processes for organic carbonates.

## ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssusche-meng.9b01390.

Transmission spectra for species in solution (PDF)

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### Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes
The authors declare no competing financial interest.

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