

# Mechanistic Study of the Electrosynthesis of Propylene Carbonate from Propylene Oxide and CO<sub>2</sub> on Copper Electrodes

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Efficient and selective electrosynthesis of propylene carbonate can be performed by the reaction of carbon dioxide with propylene oxide at copper electrodes. In this paper, we investigate this electrochemical reaction by using cyclic voltammetry, Fourier transform infrared spectroscopy and high-performance liquid chromatography in order to unravel details of the catalytic mechanism of the reaction. The combination of the results obtained by these different techniques allows the exclusion of different reduced forms of CO<sub>2</sub>, such as CO and (bi) carbonates, as possible carboxylation agents. Moreover, the results also indicate that electrochemical activation of the propylene oxide by ring opening is not the initial step for this

reaction, as no product was detected when a current was not applied in presence of “activated propylene oxide” and CO<sub>2</sub>. Our results show that the reaction is initiated by the activation of CO<sub>2</sub> to CO<sub>2</sub><sup>•-</sup>, which then attacks the epoxide to form the cyclic carbonate. This work also gives evidence for the non-catalytic nature of the synthesis of the cyclic carbonate because its formation also occurs on other metals such as gold and platinum in the same range of applied currents. This result clearly indicates the potential of in situ electrochemical techniques in the mechanistic investigation of electrosynthesis reactions.

## 1. Introduction


The accelerated increase of CO<sub>2</sub> atmospheric levels in the last decades due to the consumption of fossil fuels is causing an acute environmental problem.<sup>[1]</sup> Compared to CO<sub>2</sub> storage solutions, the fixation of CO<sub>2</sub> into organic molecules offers an attractive alternative.<sup>[2]</sup> Carbon dioxide can be used as a C1 feedstock in organic synthesis due to its abundant, cheap, renewable and non-toxic nature.<sup>[3]</sup> Among the different valuable products obtained from carbon dioxide, cyclic carbonates offer wide applications in the chemical industry. Cyclic carbonates can be utilized as fuel additives, as electrolytes for Li ion batteries, as plastics, as green reagents<sup>[4]</sup> and as raw material for the production of dimethyl carbonate,<sup>[5]</sup> which is considered as a replacement for more toxic solvents in paints and coatings since it is exempt from the restrictions placed on most volatile organic products. Many catalyst systems have been developed


for the conversion of CO<sub>2</sub> to cyclic carbonates.<sup>[6–9]</sup> High temperature and high pressure are frequently required due to the relatively low reactivity of CO<sub>2</sub>. Electrochemistry would provide an alternative manner to activate carbon dioxide at atmospheric pressure and low temperature. Electrosynthesis of cyclic carbonates has been performed under mild conditions with the achievement of an efficient and selective process.<sup>[10–12]</sup> Several metals such as copper,<sup>[12]</sup> stainless steel,<sup>[13]</sup> graphite,<sup>[13]</sup> silver<sup>[14]</sup> and nickel,<sup>[14]</sup> have been tested for the conversion of propylene oxide and CO<sub>2</sub> to propylene carbonate, obtaining the highest conversion (99%) on copper.<sup>[13]</sup> Although substantial efforts have been invested towards the achievement of a highly efficient process, the mechanism of this reaction is still under debate. Several studies attribute the opening of the propylene oxide ring as the rate-determining step, meaning that the catalyst activates the epoxide before the attack of CO<sub>2</sub>,<sup>[7–9,15,16]</sup> whereas other studies support the need of the activation of CO<sub>2</sub> as a key step to complete the reaction.<sup>[10,12,14]</sup> In this work, we study the conversion of propylene oxide and CO<sub>2</sub> to propylene carbonate (equation 1) on copper electrodes in solutions of tetraethyl ammonium perchlorate (TEAClO<sub>4</sub>) in acetonitrile by in situ Fourier transform infrared (FTIR) spectroscopy, in order to investigate these details of the mechanism of the reaction.

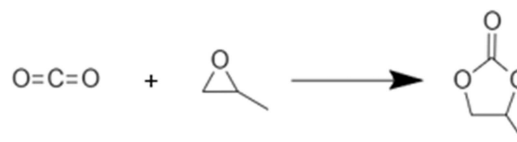
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We will show that the activation of propylene oxide can be ruled out as the rate determining step for propylene carbonate synthesis, and that the electro-activation of CO<sub>2</sub> to a CO<sub>2</sub> radical

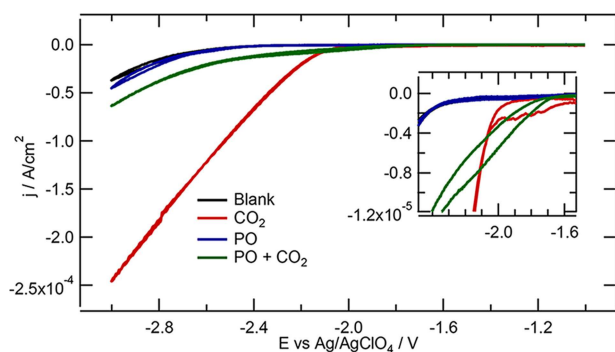
anion is the likely key step for this process. We also show that undesired by-products may be formed from the reduction of the propylene oxide and the acetonitrile solvent.

## 2. Results and Discussion

### 2.1. Cyclic Voltammetry

Figure 1 shows the cyclic voltammetry of polycrystalline copper in a 0.1 M TEAClO<sub>4</sub> solution in acetonitrile under various conditions. The voltammograms were recorded in the absence of carbon dioxide and propylene oxide PO (black curve), in the presence of propylene oxide (blue curve), in the presence of carbon dioxide (red curve) and in the presence of both propylene oxide and carbon dioxide (green curve).

The comparison between the black and blue curves in Figure 1 indicates that propylene oxide does not undergo



**Figure 1.** Cyclic voltammograms of polycrystalline copper in 0.1 M TEAClO<sub>4</sub> in acetonitrile solution in the absence of CO<sub>2</sub> and propylene oxide (black) and in the presence of CO<sub>2</sub> (red), 0.1 M propylene oxide (blue) and a combination of propylene oxide (0.1 M) and CO<sub>2</sub> (green), with Ag/AgClO<sub>4</sub> as reference electrode. Scan rate = 50 mV/s. Inset displays a zoom-in between -1.5 V and -2.5 V vs Ag/AgClO<sub>4</sub>.

significant reduction under these conditions (though FTIR measurements to be discussed below show some formation of a PO reduction product). On the other hand, when CO<sub>2</sub> is present in the solution (red curve), a reduction current is observed with an onset potential ca. -1.8 V vs. Ag/AgClO<sub>4</sub>.<sup>[17]</sup> When both propylene oxide and carbon dioxide are present in the solution (green curve), a similar onset potential as for CO<sub>2</sub> reduction is observed (red curve), but with a higher current between -1.8 and -2.2 V. This observation suggests that a reaction other than mere CO<sub>2</sub> reduction is occurring, with a faster reaction rate in the early stages of the reaction at potentials lower than -2.2 V. At more negative potentials than -2.2 V, the reaction is favored when only CO<sub>2</sub> is present. The lower reduction current observed when both substances are present in comparison with only CO<sub>2</sub> in solution suggests that the presence of propylene oxide hinders the reduction of CO<sub>2</sub>, possibly because it reacts with it to form a compound different from the reduction product of CO<sub>2</sub>. The nature of this product is characterized by FTIR and HPLC in the following section.

### 2.2. FTIR and HPLC Characterization of Intermediates and Products

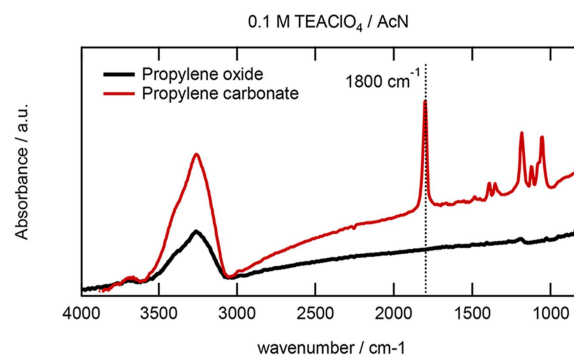
The reaction of propylene oxide with carbon dioxide on copper electrodes in TEAClO<sub>4</sub> prepared in acetonitrile solutions was analyzed by FTIR and HPLC. It is important to explain that at the outset that both experiments were performed under galvanostatic conditions at fixed applied current. However, due to the different cell configurations (specifically the thin-layer configuration used for the FTIR experiments), these applied currents cannot be easily compared. Therefore, we have collected in Table 1 the corresponding electrode potentials.

**Table 1.** Measured electrode potentials during the electrolysis of propylene oxide and CO<sub>2</sub> in the FTIR cell for different currents.

Current [mA]	Measured potential [V] vs. AgClO <sub>4</sub> / AcN
-1	-2.73
-2	-2.80
-2.5	-2.86
-3	-2.91

Figure 2 shows the transmission spectra for the reactant (PO) and for the expected product propylene carbonate (PC). The results show that PO in the acetonitrile electrolyte does not present strong IR modes that can be used for its identification, while PC clearly shows features that aid in its identification with vibrational bands at 1800, 1392, 1184, 1118 and 1053 cm<sup>-1</sup>. We note that the reported gas-phase and liquid-phase spectra of PO show bands in the 1000–1500 cm<sup>-1</sup> range,<sup>[18]</sup> but these bands are too weak (see the black spectrum in this wavenumber range in Figure 2) to be used for identification under the conditions of our experiment. The absorbance spectrum of propylene carbonate in Figure 2 shows that PC is best identified by the characteristic C=O stretching band at 1800 cm<sup>-1</sup>.

Figure 3 shows the time dependent absorbance spectra of the copper electrode in the presence of 0.1 M propylene oxide and saturated CO<sub>2</sub> atmosphere with an applied reduction current of -2.5 mA, which corresponds to an electrode



**Figure 2.** Absorbance spectra of a 0.1 M TEAClO<sub>4</sub> solution prepared in acetonitrile with 0.1 M propylene oxide (black) and with 0.1 M propylene carbonate (red). Band at 1800 cm<sup>-1</sup> indicates the C=O stretching band of propylene carbonate.

potential of  $-2.86$  V vs Ag/AgClO<sub>4</sub> (see Table 1). The assignment of the different bands was done with the help of the transmission spectra and previous reports on CO<sub>2</sub> electrochemical reduction in acetonitrile<sup>[17]</sup> and is summarized in table 2. In addition, vibrational bands for possible decomposi-

**Table 2.** Assignment of the FTIR bands.

$\nu$ [cm <sup>-1</sup> ]	Assignment	Compound
2333	s C=O	CO <sub>2</sub>
2295	s C–N	acetonitrile
2252	s C–N	acetonitrile
1800	s C=O	propylene carbonate
1731	s C=O	Possible propylene oxide decomposition product
1647	s C=O	CO <sub>3</sub> <sup>2-</sup>
1674	s C=O	acetamide (acetonitrile decomposition product)
1628	b O–H	Water
1585	s N–H	acetamide (acetonitrile decomposition product)
1481	s C–O	HCO <sub>3</sub> <sup>-</sup>
1361	s C–O	CO <sub>3</sub> <sup>2-</sup>
1334	s C–O	CO <sub>3</sub> <sup>2-</sup>
1178	s N–H	acetamide (acetonitrile decomposition product)
1110	s Cl–O	ClO <sub>4</sub> <sup>-</sup>

tion products for PO where also investigated by performing FTIR spectra of a copper electrode with a TEAClO<sub>4</sub> solution containing only propylene oxide under reductive conditions (See supporting information, SI.1). The assignment of the decomposition products is also included in Table 2.

Figure 3 displays the absorbance spectra taken at different times during the electrosynthesis of propylene carbonate from propylene oxide and carbon dioxide at an applied current of  $-2.5$  mA ( $-2.86$  V vs. Ag/AgClO<sub>4</sub>). After one minute, CO<sub>2</sub> (2333 cm<sup>-1</sup>) starts to be consumed and several bands corresponding with the formation of products start to rise at 1647, 1481, 1361 and 1334 cm<sup>-1</sup>. These latter bands can be attributed to (bi)carbonate species, CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup> and CO<sub>3</sub><sup>2-</sup> respectively, as described by Figueiredo et al.<sup>[17]</sup> Previous studies suggested that the existence of different vibrational bands for C=O and C–O bonds on bicarbonates and carbonates is due to the presence of different ion pairs of the anions with TEA<sup>+</sup> cations or solvation shells with residual water.<sup>[19]</sup> At 1110 cm<sup>-1</sup> the band corresponding to ClO<sub>4</sub><sup>-</sup> from the supporting electrolyte is also observed. At longer times (5, 9, 13 and 17 minutes), during the electroreduction of propylene oxide and carbon dioxide, the spectra show a band at 1800 cm<sup>-1</sup> growing with time. Figure 3b shows a zoom-in of the spectral region where this band is observed. The band at 1800 cm<sup>-1</sup> is attributed to the C=O stretching mode of propylene carbonate, according to the absorbance spectrum of propylene carbonate displayed in Figure 2.

Importantly, simultaneously with the band 1800 cm<sup>-1</sup>, a band at 1731 cm<sup>-1</sup> is observed. In order to evaluate if this band is due to byproducts, the absorbance spectra of several species such as ethylene glycol, 1-methoxy 2-propanol and 2-propanol were recorded (See SI.3). The absence of a band around

1731 cm<sup>-1</sup> rules out that the band comes from one of these species. Moreover, the band at 1731 cm<sup>-1</sup> does not come from a species originating from further reduction of propylene carbonate, since reduction of propylene carbonate does not lead to a band at 1731 cm<sup>-1</sup> (See SI.4). We suggest that the band at 1731 cm<sup>-1</sup> might be due to the reductive decomposition of propylene oxide. The attribution is done based on the observation that this band appears during the reduction of propylene oxide in the absence of carbon dioxide (See SI.1). However, further studies using mass spectroscopy (MS) or nuclear magnetic resonance (NMR) must be carried out to identify the nature of this species.

The electroreduction of propylene oxide and carbon dioxide on copper was also carried out at different currents as summarized in Table 1.

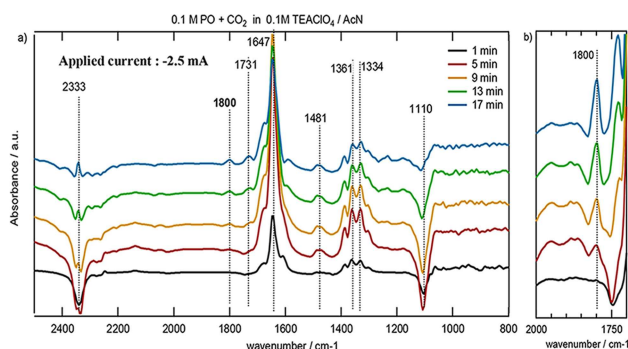
Figure 4a displays the integrated areas of the band at 1800 cm<sup>-1</sup> (attributed to propylene carbonate) as a function of the applied current and time. The formation of propylene carbonate is observed after only 5 minutes of electrolysis giving increasing product formation with time for all the different applied currents. Moreover, applying higher currents leads to more product formation.

The electroreduction of 0.1 M propylene oxide and CO<sub>2</sub> on copper was also studied by HPLC. Figure SI.2 in the Supporting information shows the time dependent HPLC chromatograms obtained during the reduction of 0.1 M propylene oxide and CO<sub>2</sub> on a copper electrode in a 0.1 M TEAClO<sub>4</sub> in acetonitrile solution at  $-2.86$  V vs. Ag/AgClO<sub>4</sub>. Different currents were applied (see Table 1) to evaluate the effect of the applied current to the formation of propylene carbonate. The percentages of propylene carbonate formed (yield) at different currents are displayed in Figure 4b as a function of time. As expected, the amount of product formed increases with time and with the applied current.

The combination of the FTIR and HPLC experiments confirm the formation of propylene carbonate from propylene oxide and carbon dioxide on copper electrodes. However, as the used organic solvents were not dry and contain residual water, reduction of water can also take place at these applied currents and potentials, leading to the generation of OH<sup>-</sup>. In order to ensure that this is an electrochemical process and not a chemical synthesis catalyzed by the presence of OH<sup>-</sup>, the spectra of propylene oxide and CO<sub>2</sub> in the presence of a strong base (TEAOH) were recorded (see SI. The spectra show an intense band at 2341 cm<sup>-1</sup> corresponding to C=O stretching from CO<sub>2</sub> in solution. Less intense bands at 1670 cm<sup>-1</sup> corresponding to decomposition products from the acetonitrile were also observed. However, the absence of a band at 1800 cm<sup>-1</sup> that would correspond to propylene carbonate, supports the electrochemical nature of the synthesis of propylene carbonate instead of a chemical reaction catalyzed by the electrogenerated OH<sup>-</sup>, in accordance with the results observed by Yang et al.<sup>[20]</sup>

### 2.3. Proposed Mechanism

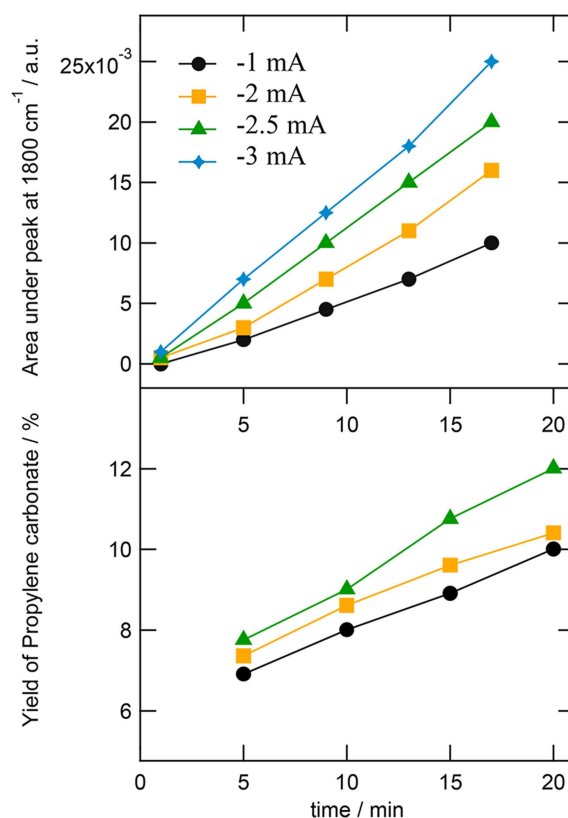
In the interest of understanding the mechanism of electrochemical formation of propylene carbonate from propylene oxide and CO<sub>2</sub> on copper, CO and carbonates (two known products from CO<sub>2</sub> electroreduction) were tested as the possible electroactive species for the synthesis of propylene carbonate. Figure SI.6 shows the time dependent absorbance spectra of copper in the presence of 0.1 M propylene oxide and saturated carbon monoxide atmosphere in 0.1 M TEAClO<sub>4</sub> in acetonitrile solution under reductive conditions. Carbon monoxide is known to be an intermediate of CO<sub>2</sub> reduction on copper electrodes in aqueous electrolytes<sup>[21–22]</sup> as well as in acetonitrile electrolyte containing small amounts of water.<sup>[17]</sup> It is also known that the catalytic reaction between CO and propylene oxide can yield propiolactone under certain conditions.<sup>[23]</sup> However, the absence of the band at 1800 cm<sup>-1</sup> (corresponding with propylene carbonate) when CO<sub>2</sub> is exchanged for CO, discards CO as the electroactive species in the mechanism of propylene carbonate formation. Previous studies of CO<sub>2</sub> reduction in non-aqueous solvents showed that the main products formed at high overpotentials are bi(carbonates).<sup>[17]</sup> In our work, (bi)carbonates were indeed formed during the electrochemical reaction of propylene oxide and CO<sub>2</sub>, identifiable by the bands observed at 1647, 1481, 1361 and 1334 cm<sup>-1</sup> in Figure 3. The bands



**Figure 3.** a) Time-dependent absorbance spectra of a copper electrode in the presence of 0.1 M propylene oxide and saturated carbon dioxide atmosphere in 0.1 M TEAClO<sub>4</sub> in acetonitrile solution at -2.5 mA after 1 minute (black), 5 min (red), 9 min (orange), 13 min (green) and 17 min (blue). b) Zoom-in of spectra shown in a) between 2000–1720 cm<sup>-1</sup>.

attributed to (bi)carbonate formation during the electroreduction of propylene oxide and CO<sub>2</sub> decrease with time (see Figure 3) while the formation of propylene carbonate (band at 1800 cm<sup>-1</sup>) increases with time. A possible explanation of these observations would be that (bi)carbonates are being formed first by reduction of CO<sub>2</sub> and then consumed by reacting with propylene oxide to form propylene carbonate.

However, when FTIR spectra were recorded using TEAHCO<sub>3</sub> in solution instead of bubbling CO<sub>2</sub>, formation of propylene carbonate was not observed (see SI. 7). Therefore, we rule out (bi)carbonates as the electroactive species for the formation of propylene carbonate on copper. The intensity decrease of the (bi)carbonates bands observed in Figure 3 at longer electrolysis



**Figure 4.** a) Area measured under the band at 1800 cm<sup>-1</sup> (corresponding to propylene carbonate) observed during the reduction of 0.1 M PO and CO<sub>2</sub> on copper in 0.1 M TEAClO<sub>4</sub> in acetonitrile solution at different currents and different times. b) Yield of propylene carbonate observed during the reduction of PO and CO<sub>2</sub> on copper in 0.1 M TEAClO<sub>4</sub> in acetonitrile solution at different current and different times.

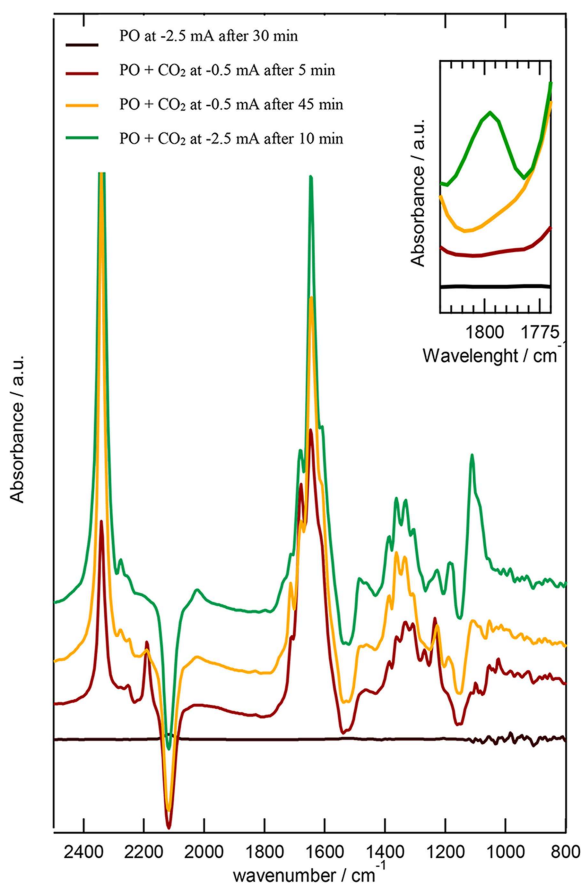
times appears to be mirrored by the increase of the intensity of the band at 2333 cm<sup>-1</sup> corresponding to the C=O stretching mode of CO<sub>2</sub>, which is no longer being reduced to (bi) carbonates. Due to the low solubility of TEAHCO<sub>3</sub> in acetonitrile, (bi)carbonates were also generated in situ by reduction of CO<sub>2</sub> on copper. After 30 minutes of electrolysis at saturated carbon dioxide atmosphere at -2.5 V vs Ag/AgClO<sub>4</sub> with the subsequent generation of (bi)carbonates, propylene oxide was added to the electrochemical cell, and a current of -2.5 mA (corresponding to -2.86 V vs. Ag/AgClO<sub>4</sub>) was applied, recording the spectra every 4 minutes (data not shown). These in situ generated (bi)carbonates also do not generate the vibrational band characteristic for propylene carbonate at 1800 cm<sup>-1</sup>. Therefore, we exclude (bi)carbonates as the electroactive species for the formation of propylene carbonate on copper electrodes.

Homogeneous catalysis studies concerning the synthesis of propylene carbonate have proposed the activation of propylene oxide<sup>[8,24]</sup> as the rate determining step, in which the catalyst induces a nucleophilic attack on the non-substituted carbon of the epoxide causing the opening of the ring. Foltran et al. proposed three possible reaction pathways:<sup>[8]</sup> (1) Catalyst and CO<sub>2</sub> acts simultaneously on the epoxide, (2) Catalyst activates the epoxide before addition of CO<sub>2</sub> and (3) Activation of CO<sub>2</sub> by



the catalyst occurs before the activation of the epoxide. Reaction paths 1 and 2 were structurally and energetically investigated by Foltran and co-workers using density functional theory (DFT),<sup>[8]</sup> from which they selected path 2, in which the catalyst activates the epoxide by ring opening before the addition of CO<sub>2</sub> as the most preferable pathway. Path 3, in which the activation of CO<sub>2</sub> by the catalyst occurs before the addition of the epoxide was not investigated due to the high energy needed to activate CO<sub>2</sub>.

The activation of propylene oxide as a required step for the synthesis of propylene carbonate on copper electrodes was evaluated in the experiment illustrated in Figure 5, which shows



**Figure 5.** Time- and current-dependent absorbance spectra of a copper electrode in the presence of propylene oxide at  $-2.5$  mA after 30 minutes (black), in the presence of propylene oxide and carbon dioxide at  $-0.5$  mA after 5 minutes (red) and after 45 minutes (yellow) and in the presence of propylene oxide and carbon monoxide at  $-2.5$  mA after 10 minutes (green). The inset displays the zoom-in of the region between  $1900$ – $1750$   $\text{cm}^{-1}$ .

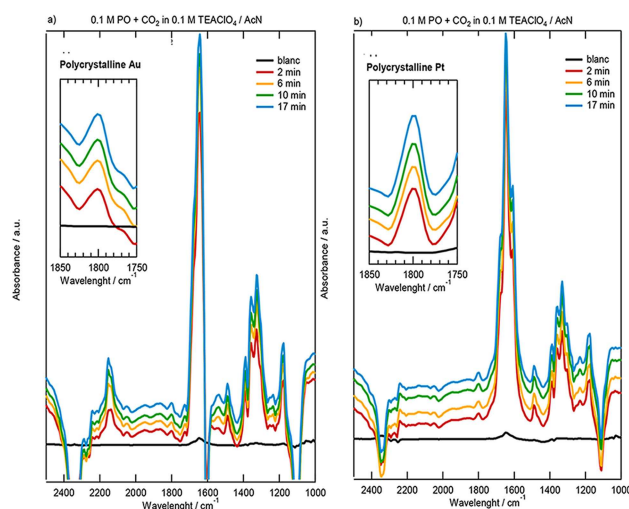
time-dependent absorbance spectra at different conditions. First, absorbance spectra were recorded after propylene oxide was reduced at  $-2.5$  mA ( $-2.86$  V vs. Ag/AgClO<sub>4</sub>) for 30 minutes (black line). This conditioning step was expected to activate the epoxide and thus lead to opening of the ring. The next step was to introduce CO<sub>2</sub> in the electrochemical cell (at a current of  $-0.5$  mA at which no propylene carbonate was observed in previous experiments) and spectra was recorded every 4

minutes for 45 minutes (red and yellow lines). If the activated propylene oxide would indeed be the active species, propylene carbonate should form after the addition of CO<sub>2</sub>. However, the absence of the band at  $1800$   $\text{cm}^{-1}$  when a mild reduction current was applied with CO<sub>2</sub> present in solution, suggests that reductive ring opening is not a critical step but rather that CO<sub>2</sub> needs to be activated. Indeed, when in the presence of CO<sub>2</sub> and propylene oxide a higher current is applied it results in the formation of propylene carbonate (green line). These experimental results suggest that under electrochemical conditions the reaction pathway starts with the activation of CO<sub>2</sub> by the electrode before the activation of the epoxide, in agreement with the conclusion of Wang et al.<sup>[14]</sup> In addition, no evidence of any substance coming from the opening of the epoxide ring prior to the formation of PC has been observed by FTIR (the band at  $1731$   $\text{cm}^{-1}$  does not appear to correspond to a ring-opening product). Therefore, we suggest the electroreduction of CO<sub>2</sub> to CO<sub>2</sub><sup>•−</sup> as a key step for the formation of propylene carbonate, in accordance with the work of Xiao et al. and Wang et al.<sup>[10,14]</sup> However, the observation of the CO<sub>2</sub> radical anion itself as an intermediate of the reaction is not easily confirmed by FTIR due to its short lifetime.

#### 2.4. Electrosynthesis of Propylene Carbonate on Other Metals

In the interest of understanding whether the process of propylene carbonate formation is an electrocatalytic reaction or simply a electrochemical process with no strong effect of the electrode material used, Au and Pt were tested as cathodes for the electrochemical conversion of propylene oxide and CO<sub>2</sub> to propylene carbonate.

Figure 6 shows the time-dependent absorbance spectra for gold (Figure 6a) and for platinum (Figure 6b) in  $0.1$  M TEAClO<sub>4</sub>, in the presence of  $0.1$  M PO and CO<sub>2</sub> atmosphere, in acetonitrile



**Figure 6.** Time-dependent absorbance spectra for a) Au and b) Pt electrodes in the presence of  $0.1$  M propylene oxide and saturated carbon dioxide atmosphere in  $0.1$  M TEAClO<sub>4</sub> in acetonitrile solution at  $-2.5$  mA. Insets display the zoom-in of the region of the spectra between  $1900$  and  $1700$   $\text{cm}^{-1}$ .

solution at an applied current of  $-2.5$  mA ( $-2.86$  V vs. Ag/AgClO<sub>4</sub>). The attribution of the bands observed are summarized in Table 1. On both electrode materials, a band at  $1800$  cm<sup>-1</sup> corresponding to the C=O stretching mode of propylene carbonate is observed. We note that the band intensities between different experiments cannot be compared quantitatively as the (thickness of the) thin layer cannot be controlled accurately between different experiments. Nevertheless, the results strongly suggest that the reaction is electrochemical and that it is not sensitive to the cathode material. Previous studies have reported the synthesis of propylene carbonate on other materials such as stainless steel<sup>[10]</sup> and nickel,<sup>[14]</sup> in agreement with the non-electrocatalytic character of this reaction.

### 3. Conclusions

The electrosynthesis of propylene carbonate from propylene oxide and carbon dioxide on copper electrodes in TEAClO<sub>4</sub> in acetonitrile solutions has been investigated by cyclic voltammetry, FTIR and HPLC. The cyclic voltammogram of copper in the presence of propylene oxide and carbon dioxide shows a reduction current attributed to the formation of propylene carbonate. The formation of propylene carbonate was confirmed by FTIR spectroscopy and HPLC, showing the expected increased product formation at longer times and higher currents. The aim of this work was to use these techniques to study the possible mechanisms suggested in the literature for the initiation of the reaction. Our results show that the reaction between propylene oxide and carbon dioxide is an electrochemical reaction, initiated by the activation of CO<sub>2</sub> to CO<sub>2</sub><sup>•-</sup>. Both CO and carbonates were ruled out as intermediates for propylene carbonate synthesis on copper due to the absence of the formation of the cyclic carbonate. Base catalysis was also ruled as a possible mechanism. Moreover, the need of propylene oxide activation via ring opening before the further attack of CO<sub>2</sub> was ruled out since no product was detected if a current was not applied in presence of "activated propylene oxide" and CO<sub>2</sub>. Therefore, the key step in the synthesis of propylene carbonate is the activation of CO<sub>2</sub> by forming the radical anion CO<sub>2</sub><sup>•-</sup>, which will attack the epoxide to form propylene carbonate. The formation of propylene carbonate also occurs on other metals such as gold and platinum, giving evidence for the non-electrocatalytic nature of the reaction.

### Experimental Section

Prior to every experiment, the glassware was boiled in MilliQ water to remove possible salts, and subsequently rinsed with acetone. Next, the glassware was then dried in the oven at  $100$  °C for 20 minutes. Electrolytes were made of tetraethyl ammonium perchlorate (Alfa Aesar, 98%) dissolved in acetonitrile (Sigma Aldrich, 99.8%). Propylene oxide (Sigma Aldrich) had a purity of 99%. The electrolyte solutions still contain ca. 50–100 ppm water.<sup>[17,25]</sup>

A flamed annealed platinum wire was used as a counter electrode, and an Ag/AgClO<sub>4</sub> in acetonitrile was used as a reference

electrode.<sup>[24]</sup> Copper disc electrodes were used as working electrode (99.99%, from Mateck). The electrodes were electropolished in a 10:5:2 solution of H<sub>3</sub>PO<sub>4</sub>:H<sub>2</sub>O:H<sub>2</sub>SO<sub>4</sub> at  $+3$  V vs. Cu for 10 s. The applied current was controlled by an Ivium A06075 potentiostat. Before every experiment, argon (Linde, 6.0) was bubbled through the electrolyte for 25 minutes to de-aerate the solution, after which CO<sub>2</sub> (Linde, 6.0) was bubbled through the solution for another 25 minutes until saturation was reached.

Fourier transform infrared spectroscopy (FTIR) was used to detect intermediates, adsorbed species and species in solution during the reaction. The measurements were performed with a Bruker Vertex 80 V Infrared spectrophotometer.<sup>[26]</sup> The electrochemical cell was assembled on top of a  $60^\circ$  CaF<sub>2</sub> prism, and the electrode was situated against this prism to form a thin layer. The measurements were performed under external reflection. FTIR spectra were obtained from an average of 100 scans with a resolution of  $8$  cm<sup>-1</sup> at selected currents every 4 minutes. The spectra are shown as  $(R-R_0)/R_0$  where  $R$  is the reflectance at the sample and  $R_0$  is the reflectance at the reference at zero current. Therefore, the ratio  $\Delta R/R_0$  gives positive bands for the formation of species near the electrode, while negative bands correspond to the loss of species. P-polarized light was used to probe species both near the electrode surface and in solution.

The experiments in the thin layer configuration have experimental limitations. As the thin layer cannot be rigorously controlled, spectra cannot be used for quantification. The intensity of the bands cannot be directly compared between experiments since different thin layers are involved. However, within a single experiment, trends in intensity are reliable semi-quantitative indicators of changes in concentration. The experiments were replicated three times, and the same trends were observed for the same conditions. We also note that the cell configurations of the FTIR and the HPLC cells are very different, so that those results cannot be compared quantitatively. The HPLC was performed primarily to aid in the identification of the products, not to claim quantitative product yields. Both FTIR and HPLC experiments were performed under galvanostatic conditions but we stress that in the FTIR thin-layer cell configuration the current distribution is highly inhomogeneous (a significant fraction of the current is in fact flowing through the back side of the electrode from which no IR light is reflected). For a more sensible and relevant comparison, we quote in Table 1 the electrode potentials corresponding to the applied current densities in the FTIR cell. We note that previous experiments by Lu et al.<sup>[12]</sup> have shown that the Faradaic yield for PC can vary between 21 to 86%, depending on the surface of the copper electrode. We expect that our flat electrode would be closer to the lower number; however, the purpose of our study was not to obtain yields, but to obtain mechanistic insights.

The electrode potential was controlled with a Potentiostat 466 System (Model ER466) from E-DAQ. All the experiments were performed at room temperature. The transmission spectra of the solution species were collected using a SeZn window with an incident angle of  $60^\circ$  and obtained by averaging 100 scans with a resolution of  $8$  cm<sup>-1</sup>.

The liquid products formed during the electrosynthesis of propylene carbonate were collected and analyzed by High Performance Liquid Chromatography (HPLC) with a RID detector (Shimadzu). A  $0.005$  M H<sub>2</sub>SO<sub>4</sub> solution was used as an eluent in an Aminex HPX-87H (Biorad) column with a flow rate of  $0.6$  mL/min. Samples were taken at different times of electrolysis carried out in a H-cell with separate cathode and anode compartments.

## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** CO<sub>2</sub> reduction · electrosynthesis · FTIR · copper · propylene carbonate

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