



Universiteit  
Leiden  
The Netherlands

## **Electroreduction of nitrate and carbon dioxide on copper electrodes: a mechanistic study**

Perez Gallent, E.

### **Citation**

Perez Gallent, E. (2018, February 1). *Electroreduction of nitrate and carbon dioxide on copper electrodes: a mechanistic study*. Retrieved from <https://hdl.handle.net/1887/61142>

Version: Not Applicable (or Unknown)

License: [Licence agreement concerning inclusion of doctoral thesis in the Institutional Repository of the University of Leiden](#)

Downloaded from: <https://hdl.handle.net/1887/61142>

**Note:** To cite this publication please use the final published version (if applicable).

Cover Page



Universiteit Leiden



The following handle holds various files of this Leiden University dissertation:

<http://hdl.handle.net/1887/61142>

**Author:** Perez Gallant, E.

**Title:** Electroreduction of nitrate and carbon dioxide on copper electrodes: a mechanistic study

**Issue Date:** 2018-02-01

## Chapter 6

# Mechanistic study of the electrosynthesis of propylene carbonate from propylene oxide and CO<sub>2</sub> on copper electrodes

---

*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 Cyclic Voltammetry (CV), Fourier Transform Infrared Spectroscopy (FTIR) and High Performance Liquid Chromatography (HPLC) in order to unravel 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 the ring opening is not the initial step for this reaction since no product was detected if a current was not applied in presence of “activated propylene oxide” and CO<sub>2</sub>. We propose an electrochemical reaction 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-electrocatalytic nature of the cyclic carbonate synthesis since the formation of propylene carbonate also occurs on other metals such as gold and platinum in the same range of applied currents. These results clearly indicate the potential of in situ electrochemical techniques in the mechanistic investigation of electrosynthesis reactions.*

---

This chapter has been submitted as : E Pérez-Gallent, MC Figueiredo, MTM Koper

## 6.1 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>39</sup>. Compared to CO<sub>2</sub> storage solutions, the fixation of CO<sub>2</sub> into organic molecules offers an attractive alternative<sup>159</sup>. Carbon dioxide can be used as a C1 feedstock in organic synthesis due to its abundant, cheap, renewable and non-toxic nature<sup>70</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>160</sup> and as raw material for the production of dimethyl carbonate<sup>69</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>72-74, 161</sup>. High temperature and high pressure are frequently required due to the relatively low reactivity of CO<sub>2</sub> at low energy input. 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>80, 84, 162</sup>. Several metals such as copper<sup>80</sup>, stainless steel<sup>79</sup>, graphite<sup>79</sup>, silver<sup>81</sup> and nickel<sup>81</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>79</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>72, 74, 83, 161, 163</sup>, whereas other studies support the need of the activation of CO<sub>2</sub> as a key step to complete the reaction<sup>80-81, 84</sup>. In this work, we study the conversion of propylene oxide and CO<sub>2</sub> to propylene carbonate on copper electrodes in tetraethyl ammonium perchlorate (TEAClO<sub>4</sub>) in

acetonitrile solutions by in situ Fourier Transform Infrared (FTIR) spectroscopy, in order to investigate the mechanism of the reaction. 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.

## **6.2 Experimental**

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%). The electrolyte solutions still contain ca. 50-100 ppm water<sup>164-165</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>165</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>128</sup>. The electrochemical cell was assembled on top of a 60° 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

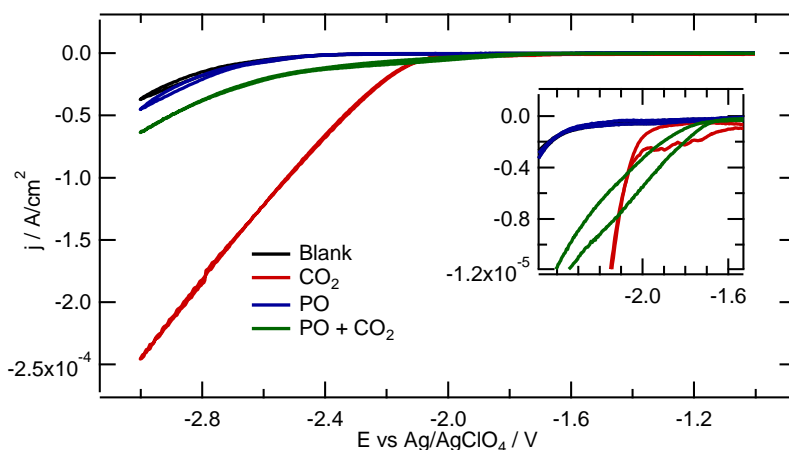
scans with a resolution of  $8\text{ cm}^{-1}$  at selected currents every 4 minutes. The spectra are shown as  $(R-R_0)/R_0$  where  $R$  is the reflectance at the sample and  $R_0$  is the reflectance at the reference at zero current. Therefore, the ratio  $\Delta R/R_0$  gives positive bands for the 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 some 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 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  $8\text{ cm}^{-1}$ .

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  $0.005\text{ M}$   $\text{H}_2\text{SO}_4$  solution was used as an eluent in an Aminex HPX-87H (Biorad) column with a flow rate of  $0.6\text{ mL/min}$ . Samples were taken at different times of electrolysis carried out in a H-cell with separate cathode and anode compartments.

## 6.3 Results and discussion

### 6.3.1 Cyclic voltammetry

Fig. 6.1 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).



**Figure 6.1:** 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>.

The comparison between the black and blue curves in Fig.6.1 indicates that propylene oxide does not undergo 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>164</sup>. When both propylene oxide and carbon dioxide are present in the solution (green curve), a similar onset potential to 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 new compound different from the reduction product of CO<sub>2</sub>.

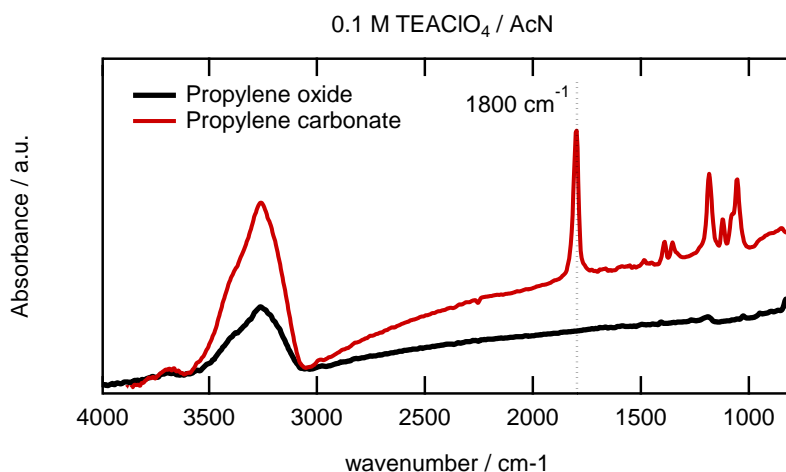
### **6.3.2 FTIR and HPLC characterization of intermediates and products**

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. Fig.6.2 shows the transmission spectra for the reactant (PO) and for the expected product propylene carbonate (PC). The results show that PO does not have any vibrational mode active in IR, while PC clearly shows features that can lead to its identification with vibrational bands at 1800, 1392, 1184, 1118 and 1053 cm<sup>-1</sup>. The absorbance spectrum of propylene carbonate in Fig. 6.2 shows that PC is best identified by the characteristic C=O stretching band at 1800 cm<sup>-1</sup>.

Fig. 6.3 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 - 5 mA cm<sup>-2</sup>. 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>164</sup> and is summarized in table 6.1. In addition,



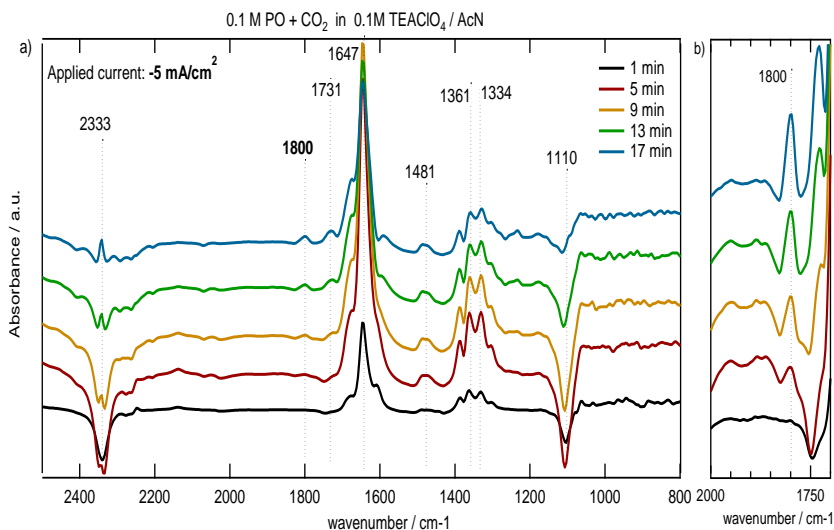
vibrational bands for possible decomposition products for PO were also investigated by performing FTIR spectra of a copper electrode with a  $\text{TEAClO}_4$  solution containing only propylene oxide under reductive conditions (data not shown). The assignment of the decomposition products is also included in Table 6.1.



**Figure 6.2:** Absorbance spectra of a 0.1 M  $\text{TEAClO}_4$  solution prepared in acetonitrile with propylene oxide (black) and with propylene carbonate (red). Band at  $1800\text{ cm}^{-1}$  indicates the  $\text{C}=\text{O}$  stretching band of propylene carbonate.

Fig. 6.3 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  $-5\text{ mA/cm}^2$ . After one minute,  $\text{CO}_2$  ( $2333\text{ cm}^{-1}$ ) starts to be consumed and several bands corresponding with the formation of products start to rise at  $1647$ ,  $1481$ ,  $1361$  and  $1334\text{ cm}^{-1}$ . These latter bands can be attributed to (bi)carbonate species,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_2^-$ ,  $\text{CO}_3^{2-}$  and  $\text{CO}_3^{2-}$  respectively, as described by Figueiredo et al.<sup>164</sup>. Previous studies suggested that the existence of different vibrational bands for  $\text{C}=\text{O}$  and  $\text{C}-\text{O}$  bonds on bicarbonates and carbonates is due to the presence of different ion pairs of the anions with  $\text{TEA}^+$  cations or solvation shells with residual water<sup>166</sup>. At longer times (5, 9, 13 and 17 minutes) during the electroreduction of propylene oxide and carbon dioxide, the

spectra show a band at  $1800\text{ cm}^{-1}$  growing with time. Fig. 3b shows a zoom-in of the spectral region where this band is observed. The band at  $1800\text{ cm}^{-1}$  is attributed to the C=O stretching mode of propylene carbonate, according to the absorbance spectra of propylene carbonate displayed in Fig. 6.2.



**Figure 6.3:** a) Time dependent absorbance spectra of a copper electrode in the presence of 0.1 M propylene oxide and saturated carbon dioxide atmosphere in 0.1M  $\text{TEAClO}_4$  in acetonitrile solution at  $-5\text{ mA/cm}^2$  after 1 minute (black), 5 minutes (red), 9 minutes (orange), 13 minutes (green) and 17 minutes (blue). b) zoom-in of spectra shown in a) between 2000-1720  $\text{cm}^{-1}$ .

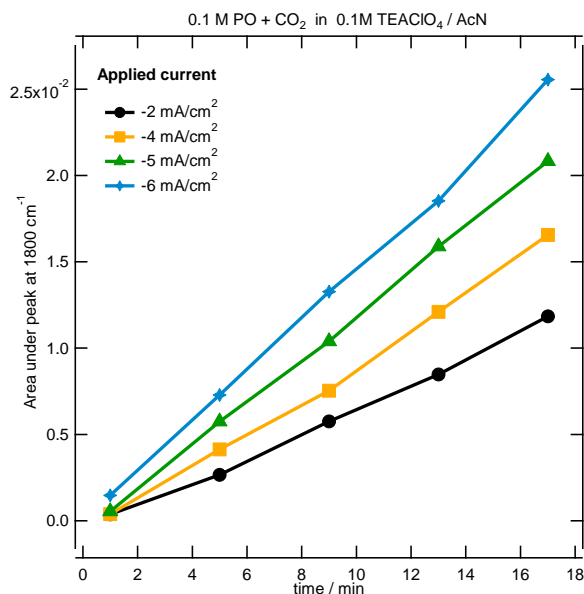
Importantly, simultaneously with the band  $1800\text{ cm}^{-1}$ , a band at  $1731\text{ cm}^{-1}$  is observed. In order to evaluate if this band is due to byproducts, the absorbance spectra of several species such as benzeneacetaldehyde, ethylene glycol, 1-methoxy 2- propanol and 2-propanol were recorded (data not shown). The absence of a band around  $1731\text{ cm}^{-1}$  rules out that the band comes from one of this species. Moreover, the band at  $1731\text{ cm}^{-1}$  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  $1731\text{ cm}^{-1}$  (data not shown). We suggest that the band at  $1731\text{ cm}^{-1}$  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. However, further studies 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 current densities (-2,-3,-4,-5 and -6 mA/cm<sup>2</sup>). Fig.6.4 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 current densities. Moreover, applying higher current densities leads to more product formation.

**Table 6.1.** Assignment of the FTIR bands

$\nu(\text{cm}^{-1})$	assignment	compound
2333	s C=O	CO <sub>2</sub>
2295	s C-N	acetonitrile
2252	s C-N	acetonitrile
<b>1800</b>	<b>s C=O</b>	<b>propylene carbonate</b>
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)
1107	s Cl-O	ClO <sub>4</sub> <sup>-</sup>

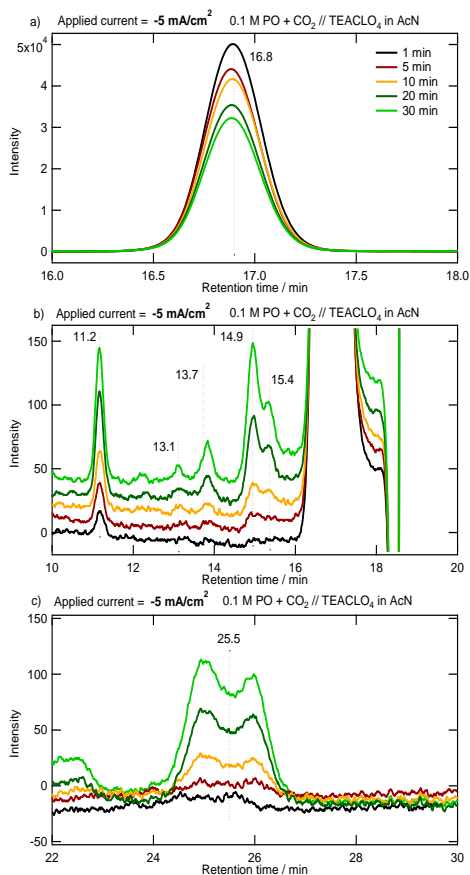


**Figure 6.4:** Area measured under the band at  $1800\text{ cm}^{-1}$  (corresponding to propylene carbonate) observed during the reduction of PO and  $\text{CO}_2$  on copper in  $0.1\text{ M TEAClO}_4$  in acetonitrile solution at different current densities and different times.

Fig. 6.5 shows the time dependent HPLC chromatograms obtained during the reduction of  $0.1\text{ M}$  propylene oxide and  $\text{CO}_2$  on a copper electrode in a  $0.1\text{ M TEAClO}_4$  in acetonitrile solution at  $-5\text{ mA/cm}^2$ . Due to large differences in peak intensities, the spectra are displayed in three different panels for a better interpretation. Fig 6.5a shows the peak corresponding to propylene oxide at  $16.8\text{ min}$ . The intensity of the peak decreases over time, indicating that propylene oxide is being consumed. Fig 6.5b shows several peaks at  $11.2, 13.1, 13.7, 14.9$  and  $15.4$  minutes. We attribute these peaks to the decomposition of propylene oxide and/or decomposition of acetonitrile. This peak attribution is based on comparison of the spectra obtained under the same conditions but in the absence of  $\text{CO}_2$  and in the absence of  $\text{CO}_2$  and propylene oxide.

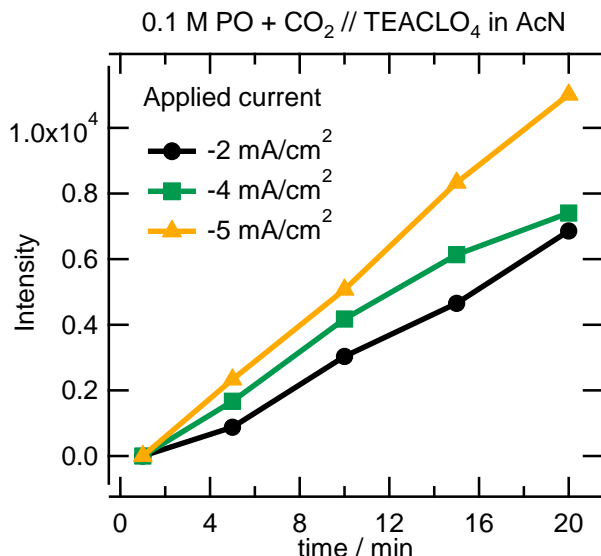
In the absence of CO<sub>2</sub>, the peaks at 11.2, 13.1 and 13.7 minutes were present, suggesting that this species results from decomposition of propylene oxide. When the spectra were recorded in the absence of CO<sub>2</sub> and propylene oxide, the peaks at 14.9 and 15.4 were present, suggesting that the species comes from the decomposition of the electrolyte. It is known that acetonitrile under reductive conditions in the presence of residual amounts of water decomposes in acetamide, as suggested by previous studies<sup>164, 167</sup>. However, the species have not been characterized with certainty and further studies would be necessary to identify them.

Finally, Fig.6.5c shows the peak attributed to the formation of propylene carbonate at 25.5 min. The double-peak nature of the peak can be tentatively attributed to different solvations of propylene carbonate. As explained before, experiments were performed in acetonitrile solutions but for the HPLC analysis, an eluent of aqueous base is used. This might cause the presence of propylene carbonate solvated by water and also solvated by acetonitrile, that will have slightly different retention times causing the split of the peak in two contributions. Nevertheless, the results show that the production of propylene carbonate during electrolysis at -5 mA/cm<sup>2</sup> increases with time. Different current densities were applied (-2 and -4 mA/cm<sup>2</sup>) to evaluate the effect of the applied current to the formation of propylene carbonate. The integrated area under the peak at 25.5 min and the applied current are displayed in Fig.6.6 as a function of time. As expected, the amount of product formed increases with time and with the applied current density.



**Figure 6.5:** Time dependent chromatograms obtained by HPLC during the reduction of 0.1 M propylene oxide and  $\text{CO}_2$  on copper in a 0.1 M  $\text{TEAClO}_4$  in acetonitrile solution at  $-5 \text{ mA/cm}^2$ . a) Displays the region between 16 and 18 minutes. b) Displays the region between 10 and 20 minutes. c) Displays the region between 22 and 30 minutes.

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  $\text{OH}^-$ . In order to ensure that this is an electrochemical process and not a chemical synthesis catalyzed by the presence of  $\text{OH}^-$ ,



**Figure 6.6:** Area measured under the peak at 25.5 minutes (corresponding to 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 densities and different times.

the spectra of propylene oxide and CO<sub>2</sub> in the presence of a strong base (TEAOH) were recorded (see appendix V, Figure AV.1). 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>78</sup>

### 6.3.3 Proposed mechanism

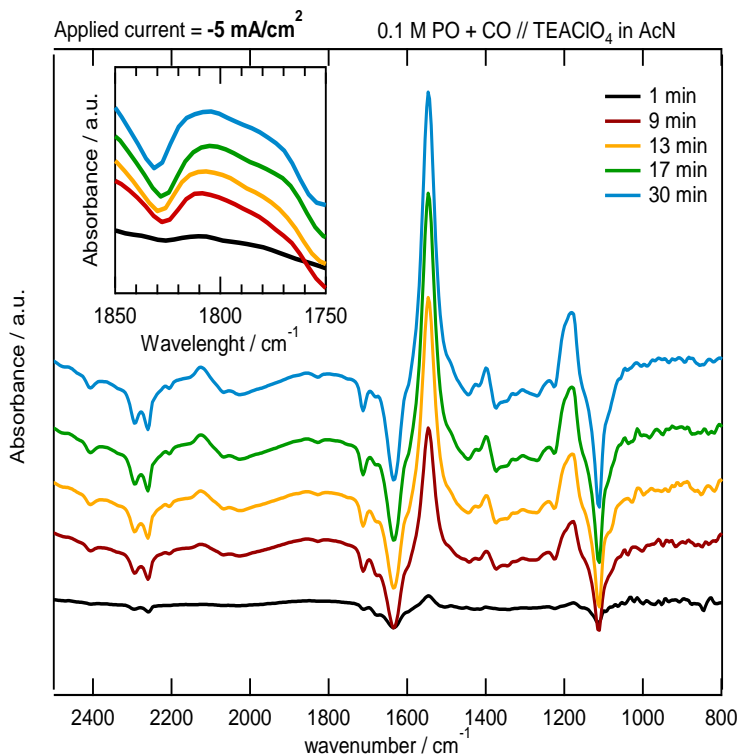
In the interest of understanding the mechanism of electrochemical formation of propylene carbonate from propylene oxide and CO<sub>2</sub> on copper, CO and carbonates (two known products from CO<sub>2</sub> electroreduction) were tested as the possible electroactive species for the synthesis of propylene carbonate.

Fig. 6.7 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 at -5 mA/cm<sup>2</sup>. Carbon monoxide is known to be an intermediate of CO<sub>2</sub> reduction on copper electrodes in aqueous electrolytes<sup>60, 168-169</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>164</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 Fig.6.3. The bands attributed to (bi)carbonate formation during the electroreduction of propylene oxide and CO<sub>2</sub> decrease with time (see Fig.6.3) 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 first formed 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 (Figure 6.8). 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

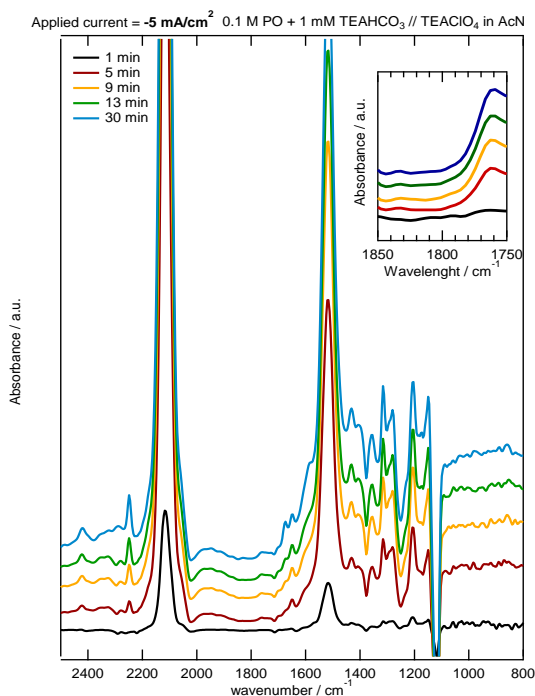




**Figure 6.7:** Time dependent absorbance spectra of copper in the presence of 0.1 M propylene oxide and saturated carbon monoxide atmosphere in 0.1M TEAClO<sub>4</sub> in acetonitrile solution at  $-5 \text{ mA/cm}^2$  after 1 minute (black), 9 minutes (red), 13 minutes (yellow), 17 minutes (green) and 30 minutes (blue). Insert displays zoom-in of the region of the spectra between 1850-1750  $\text{cm}^{-1}$ .

Fig.6.3 at longer electrolysis times appears to be mirrored by the increase of the intensity of the band at  $2333 \text{ cm}^{-1}$  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  $-2.5 \text{ V}$  vs Ag/AgClO<sub>4</sub> with the subsequent generation of (bi)carbonates,



**Figure 6.8:** Time dependent absorbance spectra of copper in the presence of 0.1 M propylene oxide and 0.01 M TEAHCO<sub>3</sub> in 0.1M TEAClO<sub>4</sub> in acetonitrile solution at  $-5 \text{ mA/cm}^2$  after 1 minute (black), 9 minutes (red), 13 minutes (yellow), 17 minutes (green) and 30 minutes (blue). Insert displays zoom-in of the region of the spectra between  $1850\text{-}1750 \text{ cm}^{-1}$ .

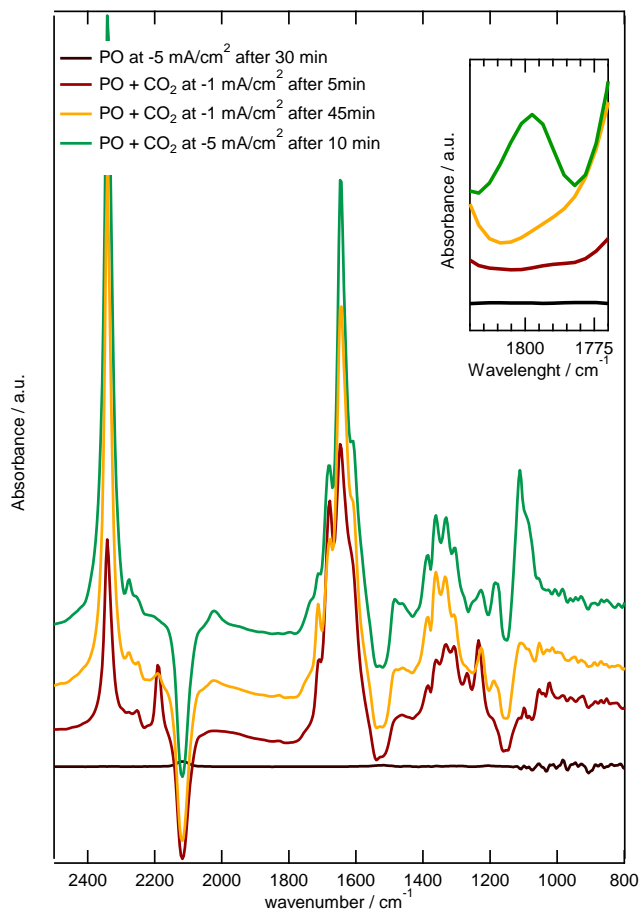
propylene oxide was added to the electrochemical cell, and a current density of  $-5 \text{ mA/cm}^2$  was applied, recording the spectra every 4 minutes (data not shown). In situ generated (bi)carbonates also do not generate the vibrational band characteristic for propylene carbonate at  $1800 \text{ cm}^{-1}$ . 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>74, 170</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>74</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 path 1 and 2 were structurally and energetically investigated by Foltran and co-workers using density functional theory (DFT) <sup>74</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 Fig 6.9, which shows time-dependent absorbance spectra at different conditions. First, absorbance spectra were recorded after propylene oxide was reduced at -5 mA/cm<sup>2</sup> for 30 minutes (black line). This first 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 density of -1 mA/cm<sup>2</sup> 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 cm<sup>-1</sup> when a mild reduction current was applied with CO<sub>2</sub> present in solution, suggests 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 (-5mA/cm<sup>2</sup>) 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>81</sup>. In addition, no evidence of any substance coming from an opening of the epoxide ring prior to the formation of PC has been observed by FTIR (the band at 1731 cm<sup>-1</sup> does not appear to correspond to a ring-

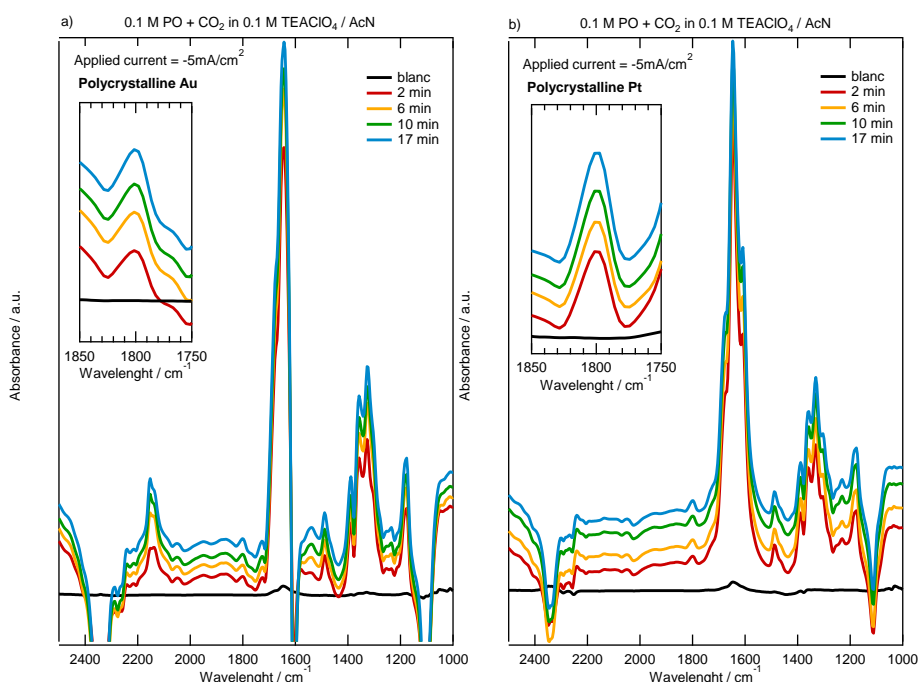
opening product). Therefore, we suggest the electroreduction of  $\text{CO}_2$  to  $\text{CO}_2^-$  as a key step for the formation of propylene carbonate, in accordance with the work of Xiao et al. and Wang et al.<sup>81,84</sup>. However, the observation of the  $\text{CO}_2$  radical anion as an intermediate of the reaction is not easily confirmed by FTIR due to its short lifetime.



**Figure 6.9:** Time- and current-dependent absorbance spectra of a copper electrode in the presence of propylene oxide at  $-5 \text{ mA/cm}^2$  after 30 minutes (black), in the presence of propylene oxide and carbon dioxide at  $-1 \text{ mA/cm}^2$  after 5 minutes (red) and after 45 minutes (yellow) and in the presence of propylene oxide and carbon monoxide at  $-5 \text{ mA/cm}^2$  after 10 minutes (green). The inset displays the zoom-in of the region between  $1900 - 1750 \text{ cm}^{-1}$ .

### 6.3.3 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  $\text{CO}_2$  to propylene carbonate.



**Figure 6.10:** Time-dependent absorbance spectra for a) Au and b) Pt in the presence of 0.1 M propylene oxide and saturated carbon dioxide atmosphere in 0.1M  $\text{TEAClO}_4$  in acetonitrile solution at  $-5 \text{ mA/cm}^2$ . Inserts display the zoom-in of the region of the spectra between 1900 and 1700  $\text{cm}^{-1}$ .

Fig.6.10 shows the time-dependent absorbance spectra for gold (Fig.6.10a) and for platinum (Fig.6.10b) in 0.1M  $\text{TEAClO}_4$ , in the presence of 0.1 M PO and  $\text{CO}_2$  atmosphere, in acetonitrile solution at an applied current of  $-5 \text{ mA/cm}^2$ . The attribution of the bands observed are

summarized in Table 6.1. On both electrode materials, a band at  $1800\text{cm}^{-1}$  corresponding to the C=O stretching mode of propylene carbonate is observed. The results suggest that the reaction is electrochemical but 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>84</sup> and nickel<sup>81</sup>, in agreement with the non-electrocatalytic character of this reaction.

## 6.4 Conclusion

The electrosynthesis of propylene carbonate from propylene oxide and carbon dioxide on copper electrodes in  $\text{TEAClO}_4$  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 reaction between propylene oxide and carbon dioxide is an electrochemical reaction, initiated by the activation of  $\text{CO}_2$  to  $\text{CO}_2^-$ . 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  $\text{CO}_2$  was ruled out since no product was detected if a current was not applied in presence of “activated propylene oxide” and  $\text{CO}_2$ . Therefore, we suggest that the key step in the synthesis of propylene carbonate is the activation of  $\text{CO}_2$  by forming the radical anion  $\text{CO}_2^-$ , 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.