Integrating CO\textsubscript{2} capture with electrochemical conversion using amine based capture solvents as electrolytes

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Abstract

Carbon dioxide (CO\textsubscript{2}) is currently considered as a waste material due to its negative impact on the environment. However, it is possible to create value from CO\textsubscript{2} by capturing and utilizing it as a building block for commodity chemicals. Electrochemical conversion of CO\textsubscript{2} has excellent potential for reducing greenhouse gas emissions and reaching the Paris agreement goal of zero net emissions by 2050. To date, Carbon Capture and Utilization (CCU) technologies (i.e. capture and conversion) have been studied independently. In this communication, we report a novel methodology based on the integration of CO\textsubscript{2} capture and conversion by the direct utilization of a CO\textsubscript{2} capture media as electrolyte for electrochemical conversion of CO\textsubscript{2}. This has a high potential for reducing capital and operational cost when compared to traditional methodologies (i.e. capture, desorption and then utilization). A novel mixture of chemical and physical absorption solvents allowed for the captured CO\textsubscript{2} to be converted to formic acid with faradaic efficiencies up to 50\% and with carbon conversion of ca. 30\%. By increasing the temperature in the electrochemical reactor from 20 °C to 75 °C, the productivity towards formic acid increased by a factor of 10, reaching up to 0.7 mmol m\textsuperscript{-2} s\textsuperscript{-1}. The direct conversion of captured CO\textsubscript{2} was also demonstrated for carbon monoxide formation with faradaic efficiencies up 45\%. 

Introduction

The abrupt increase of CO\textsubscript{2} emissions into the atmosphere due to the use of fossil fuels creates adverse effects in the environment\textsuperscript{1,2}. It is imperative that measures are implemented to drastically lower these emissions in pursuance of the Paris agreement. To date, many strategies have been contemplated with the ambition of achieving this purpose. Carbon capture and sequestration (CCS)\textsuperscript{3-5}, where CO\textsubscript{2} is captured from industrial sources and stored underground, is and will remain, an important approach to diminishing atmospheric CO\textsubscript{2} concentrations. Carbon capture can be considered a mature technology and has been used in a broad variety of industrial applications. Despite the high technology readiness of the technology, extensive studies are still being carried out to improve its economical feasibility and reduce the environmental footprint. For example, solvents which demand lower energy input, lead to less corrosion, and which undergo minimal thermal or oxidative degradation are being sought\textsuperscript{6-8}. However, sequestration of captured carbon dioxide is still under debate due to its mid-term solution character, such as its limitation to areas where CO\textsubscript{2} can be stored underground and its
unprofitability\textsuperscript{9,10}. An approach with a strategic long-term vision is CO\textsubscript{2} capture and utilization (CCU), where the captured CO\textsubscript{2} is used as a feedstock for the production of valuable chemicals. This approach creates value for CO\textsubscript{2}, leading to new value chains, and forming a stepping stone towards a circular carbon economy while realizing a sustainable way of reducing atmospheric CO\textsubscript{2} concentration. To date, studies have approached CO\textsubscript{2} capture\textsuperscript{5,6,11-14} and conversion\textsuperscript{15-20} independently, whereas the strategy of this study was the integration of these two processes.

Electrochemical conversion of CO\textsubscript{2} can be considered an efficient strategy for CO\textsubscript{2} utilization due to the mild operating conditions and the possibility of tailor-made reaction pathways\textsuperscript{17}. Preliminary techno-economic analysis has determined that the most economically viable products from CO\textsubscript{2} are those where only 2 electron transfers are involved, such as carbon monoxide or formate\textsuperscript{21}. Nevertheless, several hurdles need to be overcome in order to industrialize the electrochemical conversion of CO\textsubscript{2}\textsuperscript{22}. One of the most significant challenges is related to the poor solubility of CO\textsubscript{2}\textsuperscript{23} in the electrolyte, leading to mass transfer limitations which limit current densities and reduce overall reaction efficiencies\textsuperscript{24,25}.

Several strategies to increase the productivity of added-value chemicals from CO\textsubscript{2} have been investigated, such as the use of gas diffusion electrodes (GDE)\textsuperscript{26-28}, the use of elevated pressures\textsuperscript{29,30} and the use of non-aqueous electrolytes\textsuperscript{31,32} in order to increase the availability of the gas reactant at the electrochemical surface. However, from a complete system approach, the CO\textsubscript{2} capture step is still required for the overall process. Therefore, this study proposed an integrated approach where CO\textsubscript{2} capture and conversion are combined by using the capturing media as an electrolyte for the electrochemical conversion process. The use of CO\textsubscript{2} capture solvents as electrolytes can overcome the above-mentioned limitations of a conventional electrochemical system by allowing the absorbed CO\textsubscript{2} to be feed into the electrolyzer at high concentration, thereby decreasing mass transfer limitations and increasing overall process efficiency\textsuperscript{33}. Additionally, this integrated approach offers the benefit of removing the CO\textsubscript{2} purification step – a desorption column – from in the conventional capture process. CO\textsubscript{2} desorption is energy intensive and therefore expensive, so substituting this with a direct (electrochemical) conversion step leads to an improvement of the economic feasibility of the overall integrated process\textsuperscript{34,35}. Jens et. al. assessed cost saving by integrating CO\textsubscript{2} capture with utilization and concluded that with an upstream higher than 30 mol % CO\textsubscript{2}, 46% savings in energy demand can be achieved when compared to a process without integration\textsuperscript{36}. Figure 1 shows a schematic representation of the two possible routes for CCU technologies: conventional decoupled CO\textsubscript{2} capture and conversion, and integrated CO\textsubscript{2} capture and conversion.
In the frame of CCU, the integration of CO₂ capture with CO₂ conversion must be addressed at the early development stage since a synergy between them is of paramount importance. Therefore, the selection of a capture medium should be appraised together with the compatibility assessment of that medium as electrolyte for electrochemical conversion. Finding suitable solutions for both capture and conversion processes will lead to a more robust system for the reduction of CO₂ emissions.

A limited number of studies have addressed the use of CO₂ capturing media for further electrochemical conversion. Chen et al. studied the electrochemical conversion of CO₂ in a monoethanolamine (MEA) containing solution. However, a constant feed of gaseous CO₂ was required as reduction of the captured CO₂ species was not observed. Diaz et al. reported, for the first time, the reduction of CO₂ to CO in switchable polarity solvents which can also be used for CO₂ capture. However, this study showed low faradaic efficiencies towards CO (ca. 20%), partially due to the aqueous nature of the solvent.

This study proposes a novel methodology that integrates CO₂ capture and conversion using a mixture of chemical and physical CO₂ absorption solvents as electrolytes. This presents the benefit of the abatement of continuous CO₂ feeding as a source of free CO₂. More specifically, it comprises the reduction of CO₂ towards formic acid, glycolic acid, oxalic acid and carbon monoxide in a mixture of 2-amino-2-methyl-1-propanol (AMP) and propylene carbonate (PC) solution. The presented technology comprises the in situ liberation of the captured CO₂ in the electrolyzer by increasing the temperature of the electrolyte in the vicinity of the electrode. This technology utilizes the inherent elevated temperature that is reached in electrolyzers at industrial scale due to the ohmic losses of the electrochemical system, thereby benefiting from what at first consideration might be perceived a drawback in the process.
**Proposed system**

The proposed integrated CO\(_2\) capture and conversion system comprises of three main steps: absorption of CO\(_2\) in the chemical capture solvent, liberation of the absorbed CO\(_2\) inside the electrolyzer, and electrochemical conversion of the in-situ liberated CO\(_2\).

The most developed and extensively utilized capture solvents for CO\(_2\) are those based on thermally regenerable solvents such as MEA or AMP, among others\(^3\)\. In the capture step, CO\(_2\) reacts exothermically with non-hindered primary and secondary amines to form a carbamate-species according to Eq 1. In the presence of water, due to the steric hindrance of AMP, bicarbonate is formed according to Eq 2.

\[
O=\overset{\text{primary or secondary amine}}{\text{C}}=\overset{\text{carbamate}}{\text{O}} + 2 \overset{\text{R'}}{\text{HN}} \overset{R}{\rightleftharpoons} [\overset{\text{R'}}{\text{O}}-\overset{\text{R}}{\text{C-N}}-\overset{\text{R'}}{\text{O}}] + \overset{\text{R'}}{\text{HN-H}} (1)
\]

\[
\overset{\text{RR'}}{\text{NCOO}}^- + \overset{\text{H}_2\text{O}}{} \rightleftharpoons \overset{\text{RR'}}{\text{NH}} + \overset{\text{HCO}}{\text{O}}^- (2)
\]

In the absence of water, for each mol of AMP used, 0.5 mol of carbamate is formed, resulting in a theoretical CO\(_2\) absorption of 22 g/L when a 1 M AMP solution is used\(^4\). This CO\(_2\) loading capacity is considerably higher than the absorption capacity of aqueous solutions at ambient conditions (ca. 1.5 gr/L).

In a conventional CO\(_2\) capture unit, the enriched CO\(_2\) solution is introduced into a stripper where, by the addition of thermal energy, the complexation is reversed, leading to the liberation of CO\(_2\) and the generation of lean capture solvent. However, in the proposed technology, the solvent with the carbamate/bicarbonate species is feed into the cathodic side of an electrochemical reactor where the captured CO\(_2\) is desorbed in the vicinity of the electrode surface, as a result of the equilibrium reaction (eq 1). In order to promote the in situ liberation of CO\(_2\), the electrochemical reactor is maintained at an elevated temperature (~75 °C). This mild temperature increase can easily be reached inside industrial size electrochemical reactors due to the associated ohmic losses of the electrochemical process which translate into heat.

The liberated CO\(_2\) is then electrochemically converted to formic acid, carbon monoxide or oxalic acid on the cathode according to Eq. 3-5, thereby shifting the equilibria in equation (1) back to the regeneration of the amine.

\[
\text{CO}_2 + 2 \overset{\text{H}^+}{\text{H}} + 2 \overset{\text{e}^-}{\text{e}^-} \rightarrow \text{HCOOH} \quad (3)
\]

\[
\text{CO}_2 + 2 \overset{\text{H}^+}{\text{H}} + 2 \overset{\text{e}^-}{\text{e}^-} \rightarrow \text{CO} + \overset{\text{H}_2\text{O}}{} \quad (4)
\]
\[2 \text{CO}_2 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow 2 \text{H}_2\text{C}_2\text{O}_4\] (5)

The anodic reaction is based on water oxidation to oxygen according to Eq. 6.

\[2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-\] (6)

According to these equations, the presence of protons is essential for \(\text{CO}_2\) conversion. This can arise from two different sources. Firstly, in the trace amounts of water in the catholyte as a result of proton transfer through the cationic exchange membrane (CEM) that separates anolyte and catholyte compartments. The water content before and during electrolysis was measured with titration and it was found to increase with time due to diffusion through the membrane (See section 1 in the supporting information). Higher water content was measured in the catholyte when electrolysis experiments were carried out at 75 °C versus 20 °C (See Figure S.1 in the Supporting Information). Secondly, the protonated amine counterion which is formed in situ with the carbamate species. This was proposed by Chen et.al.\textsuperscript{37} for \(\text{CO}_2\) reduction in MEA according to Eq. 7. However, it should be noted that if protons are abundant in solution, the competitive Hydrogen Evolution Reaction (HER) might be expected to dominate and the selectivity towards the desired products might be negatively affected.

\[\text{CO}_2^{-*} + [\text{AMPH}]^+ + \text{e}^- \leftrightarrow [\text{HCOO}]^- + \text{AMP}\] (7)

Following reaction, the regenerated amine solution with residual unconverted \(\text{CO}_2\) exiting the electrolyzer can then be introduced in the absorber column to capture \(\text{CO}_2\), thereby recycling the capture solvent. It is important to note that in the proposed system where a liquid product is formed (e.g. formic acid) prior recycling of the capture solvent a separation and purification step is needed in order to remove the \(\text{CO}_2\) reduction product and traces of water from the solvent.

**Results and discussion**

Cyclic voltammetry measurements were carried out to evaluate the viability of \(\text{CO}_2\) reduction in the capture media. Figure 2 shows the cyclic voltammograms performed on a Pb electrode in PC solution in the presence and absence of capture media (AMP), and in the presence of captured \(\text{CO}_2\), at different temperatures.
When CO$_2$ is added to the electrolyte, a reduction current which was not present in the blank is observed with an onset potential of -2 V vs Ag/AgCl. However, if the electrolyte is flushed with nitrogen gas to remove non-complexed CO$_2$, the current density profile is very similar to that measured for the solution without CO$_2$ (blank). This indicates reduction barely occurs, suggesting that the carbamate/bicarbonate species are not themselves directly reduced. Interestingly, when the temperature of the electrolyte is raised to 45 °C, a reduction current is observed with an onset potential of -2 V vs Ag/AgCl. This result suggests that when the temperature is increased, the desorbed CO$_2$ from the carbamate species undergoes electrochemical reduction. When the temperature of the electrolyte is increased to 75 °C, a considerably higher current is observed with an onset potential of -1.8 V vs Ag/AgCl. The higher current observed at 75 °C compared to 45 °C can be explained by increased CO$_2$ desorption at the higher temperature. It is important to mention that the CO$_2$ preloaded electrolyte forms a biphasic system at ambient temperatures, while at temperatures above 60 °C the system is monophasic. The higher solubility of carbamates at higher temperature and the lower viscosity of the solution enhances the mass transfer.

In order to shed light onto the nature of the formed reduction products and to better comprehend the effect of the temperature during the electrochemical reduction of the captured CO$_2$, chronoamperometric studies were carried out at a constant potential of -2.5 V vs Ag/AgCl on a Pb electrode at different temperatures (Figure 3). In accordance with the cyclic voltammetry results, the current density measured during electrolysis substantially increased when the electrolyte temperature was increased, rising from -3.9 mA/cm$^2$ at 15 °C to -25 mA/cm$^2$ at 75 °C.
After 5 hours of electrolysis, three different products were detected in the liquid phase: formic, glycolic and oxalic acids. The productivity for these products was higher at higher electrolyte temperatures, being significantly higher for formic acid. The productivity to formic acid increased 10 times when the temperature was raised from 15 °C to 75 °C (reaching 0.56 mmol/m²·s). Interestingly, the faradaic efficiency is relatively independent of the temperature. Moreover, it is important to note that high faradaic efficiencies towards formic acid (40%) were observed at 75 °C, while also showing high formic acid productivity (0.56 mmol/m²·s). For comparison, Alvarez-Guerra et al. showed a maximum productivity for formate on Pb electrodes in aqueous bicarbonate solution of ca. 0.35 mmol/m²·s with a Faradaic efficiency of ca. 30%\(^{41}\). Although they also reported higher faradaic efficiencies for formate production (ca. 80%), the productivity of formate at this high faradaic efficiency is only ca. 0.075 mmol/m²·s, with a low current density of 2.5 mA/cm\(^2\).

**Figure 3.** a) Chronoamperometry at -2.5 V vs Ag/AgCl on Pb electrode in a 0.7 M TEACl in PC solution containing 1M AMP preloaded with CO\(_2\) as a function of time at different temperatures (15, 45 and 75 °C). b) Productivity of formic acid, glycolic acid and oxalic acid as a function of the temperature during electrolysis at -2.5 V vs Ag/AgCl. c) Average faradaic efficiency during electrolysis at -2.5 V vs Ag/AgCl of formic acid, glycolic acid and oxalic acid as a function of the temperature.

In order to assess the importance of the organic solvent (propylene carbonate) as opposed to water, a control experiment was carried out on a 1M AMP aqueous solution (see Figure S.2 in Supporting Information). When electrolysis was performed at -2.5 V vs Ag/AgCl on a Pb electrode in a CO\(_2\) saturated 1M AMP aqueous solution at 75 °C, a high current density was measured (ca. -
40 mA/cm²). However, low faradaic efficiencies towards formic acid were observed (ca. 13 % after 1 h of electrolysis and ca. 3 % after 5 h of electrolysis). The high current densities can be attributed to the competitive reduction reaction, namely HER, due to the increased temperatures promoting this reaction when water is present. As such, exchanging the organic solvent with water results in a significant negative effect on the selectivity of the reaction, reducing the efficiency of formic acid formation by ca. 70%.

The CO₂ concentration (α) in the solvent mixture was measured before and during electrolysis using the so-called BaCO₃ precipitation method as described by Li et. al.⁴² and Santos et. al.⁴³. Figure 4 shows the CO₂ loading (moles of CO₂/moles AMP) as a function of time at different electrolysis temperatures. The maximum CO₂ loading achieved prior to reaction was ca. 0.35 mol CO₂/mol AMP, decreasing over time as a result of the desorption of CO₂ during the equilibrium reaction (1). The CO₂ loading decreases sharply in time as the temperature of the electrolyte is increased, indicating a faster CO₂ desorption rate at higher temperatures. After 5 h, the CO₂ loading is ca. 10% of the initial value when electrolysis is performed at 75 °C and ca. 93.5 % of the initial value when performed at 15 °C.

Figure 4. CO₂ loading measured during electrolysis at -2.5 V vs Ag/AgCl on Pb electrode in a 0.7 M TEACl in PC solution containing 1M AMP preloaded with CO₂ as a function of time at different temperatures (15, 45 and 75 °C) as a function of time. CO₂ loading refers to all the CO₂ loading species including carbamates and bicarbonates.

The conversion of the liberated CO₂ is shown in Figure 5a and it was calculated as:

\[
\text{CO}_2 \text{ conversion } \% = \frac{n_{\text{CO}_2 \text{ converted}}}{n_{\text{CO}_2 \text{ liberated}}} \times 100
\]

Where \(n_{\text{CO}_2 \text{ converted}}\) was calculated as:
\[CO_2 \text{ converted} = \sum_j v_j^{CO_2} \cdot n_{pj}\]

Where \(v_j^{CO_2}\) is the CO\(_2\) stochiometric coefficient for the formation of formic acid (\(j_1\)), glycolic acid (\(j_2\)) and oxalic acid (\(j_3\)) from CO\(_2\) and \(n_{pj}\) is the formed moles of products.

\(n_{CO_2 \text{ liberated}}\) was calculated as:

\[CO_2 \text{ liberated} = n_{CO_2 \text{ initial}}^{CO_2} - n_{CO_2 \text{ final}}^{CO_2}\]

Where \(n_{CO_2 \text{ initial}}^{CO_2}\) is the moles of CO\(_2\) captured in 1 M AMP in PC solution before electrolysis and \(n_{CO_2 \text{ final}}^{CO_2}\) is the moles of residual captured CO\(_2\) after a given electrolysis time.

The amount of CO\(_2\) liberated (Figure 5b) at 75 °C after 5 h is approximately 7 times higher than at 15 °C. Correspondingly, the amount of CO\(_2\) converted after 5 h of electrolysis at 75 °C is 8 times higher than at 15 °C (Figure 5c). Importantly, the highest conversion after 5 hours of electrolysis (ca. 30 \%) was achieved when the electrolyte was kept at 45 °C (Figure 5a) due to there being a better balance between the amount of CO\(_2\) liberated and that being converted. It is important to note that the electrolysis was carried out in an open system, therefore, all the desorbed CO\(_2\) that didn’t react was vented out of the system. Thereby, closing the system and operating it at elevated pressures, would allow non-converted CO\(_2\) to be absorbed again increasing the conversion.

The increase of temperature required to desorb the CO\(_2\) from the capture solvent might at first seem an extra operational cost for the system, however, when electrolysis is carried out at higher current densities and/or in a stack reactor, the inherent ohmic losses\(^{44}\) associated with the electrochemical reaction are converted into heat. These are usually seen as a disadvantage, however, with the current integrated CO\(_2\) capture and conversion strategy, they can now be advantageously utilized to improve the electrolysis process.
**Figure 5.** a) CO$_2$ conversion on a Pb electrode in a 1M AMP in PC solution as a function of time and temperature, b) Moles of CO$_2$ liberated from a 1M AMP in PC solution as a function of time and temperature, c) Moles of CO$_2$ converted on a Pb electrode in a 1M AMP in PC solution as a function of time and temperature.

**Effect of the capture solvent concentration**

The concentration of the capture solvent (AMP) was varied between 0 M and 3 M in order to understand its influence on the electrolyte solution during CO$_2$ reduction. Figure 6 shows the current density, productivity and faradaic efficiency towards formic acid, glycolic acid and oxalic acid, obtained on a Pb electrode during electrolysis at -2.5 V vs Ag/AgCl at 75 °C, as a function of the concentration of AMP in PC, in a CO$_2$ pre-saturated solution of the two. The current density increased from -10 to -25 mA/cm$^2$ when the concentration of AMP was increased from 0 M to 1 M, reaching a plateau between 1 and 2 M AMP, and decreasing to -20 mA/cm$^2$ in 3M AMP. The maximum faradaic efficiency (ca. 50%) and productivity (ca. 0.7 mmol m$^{-2}$s$^{-1}$) of formic acid was observed when a concentration of 2 M AMP in PC was used. Interestingly, increasing capture solvent concentration also leads to a decrease in current densities, faradaic efficiency and productivity of formic acid. This lower efficiency may be explained due to the higher viscosity of the 3M AMP solution, giving rise to mass transfer limitations, as well as the lower conductivity of the solution, potentially leading to current limitations (See Table 1 in the Supporting Information). The higher viscosity might be explained due to the higher levels of carbamate due to the higher loading capacity of the solution and the low solubility of the carbamate species in PC.

Importantly, the faradaic efficiency and the productivity of oxalic acid is drastically increased when low levels/no AMP are present in the electrolyte solution. The highest faradaic efficiency towards oxalic acid
was 80%, measured after 1 hour of electrolysis in the absence of AMP. However, the faradaic efficiency towards oxalic acid decreased over time reaching ca. 20% after 5 hours of electrolysis due to the decrease in available CO₂ (see Figure S.3 in the Supporting Information). While the results shown in Figure 6 are an average of five hours of electrolysis, faradaic efficiencies varied with time. Detailed information about their evolution over time as a function of the concentration of AMP and water content can be found in section 3 of the Supporting Information.

In general terms, it is clear that the nature of the electrolyte solution and the presence or absence of capture solvent significantly influences the product distribution.

**Figure 6.** a) Average current density measured over 5 hours of electrolysis at -2.5 V vs Ag/AgCl at 75 °C on Pb electrode in a CO₂ preloaded 0.7 M TEA⁺Cl⁻ in PC solution containing different concentrations of AMP (0, 0.5, 1, 2 and 3 M). b) Productivity of formic acid, glycolic acid and oxalic acid as a function of the concentration of AMP during electrolysis at -2.5 V vs Ag/AgCl at 75 °C. c) Average faradaic efficiency during electrolysis at -2.5 V vs Ag/AgCl at 75 °C of formic acid, glycolic acid and oxalic acid as a function of the concentration of AMP.

**Formic acid and CO formation in a continuous flow cell**

In order to make the first steps towards validating the proposed integrated CO₂ carbon and conversion methodology for larger-scale production, on route to commercial implementation, the technology was transferred from batch to a scalable, (semi-)continuous reactor concept. Electrochemical reduction of a CO₂ saturated 1M AMP in PC solution was carried out using an electrochemical flow cell in which the
electrolyte was continuously circulated through the reactor (See Figure 7a). In order to promote desorption of CO_2 in the vicinity of the electrode, a heating chamber was placed on the back of the metallic electrode, maintaining an electrode temperature of 75 °C during reaction. The results of these experiments (See Figure 7 b and c), using a Pb electrode, are similar results to those obtained in batch mode (see Figure 6). Only a slight increase in current density and a slight decrease in faradaic efficiency towards formic acid were observed. More details can be found in Section 4 in the Supporting information.

Additionally, a different cathode material (Au) was investigated for CO_2 reduction in the (semi-)continuous reactor concept, with the goal of extending the methodology to include the production of alternative products. It is known that in aqueous solutions, Au selectively reduces CO_2 to CO\(^{15}\). During electrochemical reduction in a 1M AMP in PC solution preloaded with CO_2 using a Au cathode, carbon monoxide was observed as the main product. Figure 7 d and e show the current density and the faradaic efficiency towards CO during electrolysis at different potentials. The highest faradaic efficiency towards CO (ca. 45%) was obtained when the electrolysis was carried out at -1.6 V vs Ag/AgCl with a current density of ca. -15 mA/cm\(^2\).

Further research to optimize the system, including the electrolyte composition and process conditions, is currently being carried out in our laboratories. Nevertheless, these results indicate the viability of implementing the proposed integrated CO_2 capture and conversion system in a continuous process and shows its potential for the reduction of captured CO_2 towards added-value chemicals such as formic acid or CO.
Figure 7. a) Electrochemical flow cell employed for CO$_2$ conversion electrolysis on Pb electrodes (b and c) and on Au electrodes (d and e). b) current density and c) Faradaic efficiency towards formic acid, glycolic acid and oxalic acid measured during electrolysis at 75 °C on Pb electrode at -2.5 V vs Ag/AgCl in a 1M AMP in PC, preloaded with CO$_2$. d) current density and e) Faradaic efficiency towards CO measured during electrolysis on Au electrode at -1.4, -1.6, -1.8 and -2 V vs Ag/AgCl in a 1M AMP in PC, preloaded with CO$_2$. 
Conclusions

This study demonstrates the feasibility of an integrated CO$_2$ capture and conversion system, where a mixture of chemical and physical absorption solvents used for CO$_2$ capture can be used as electrolyte in an electrochemical reactor to efficiently convert CO$_2$ into formic acid and CO.

This novel methodology is based on the liberation of the captured CO$_2$ inside the electrochemical reactor by increasing the temperature of the system. An increase of temperature is an inherent trait of an electrochemical system, since the ohmic losses associated to the process lead to an increase of temperature. When a mixture of 1 M AMP in PC was used as CO$_2$ capture media and afterwards as electrolyte, CO$_2$ conversion towards formic acid was achieved with faradaic efficiencies of ca. 45 % and productivity of 0.56 mmol/m$^2$·s when the process was carried out at 75 °C. The productivity of the integrated process significantly improved when increasing the temperature from 15 °C to 75 °C. This increase in productivity is associated to the preponderant liberation of CO$_2$ at elevated temperatures being 8 times higher at 75 °C than at 15 °C.

The selection of an adequate electrolyte composition is essential for the selective formation of the desired product. For instance: substituting the physical solvent (PC) for water lead to a 70 % decrease of formic acid production due to the higher production of hydrogen in aqueous media, while electrolysis in the absence of the capturing media (AMP) lead primarily to oxalic acid formation instead of formic acid. Importantly, doubling the concentration of the capture solvent to 2 M showed an improvement on the efficiency reaching 50 % and an improvement of the productivity of formic acid which reached 0.7 mmol/m$^2$·s. However, higher concentrations of AMP led to a decrease in the formic acid productivity and efficiency, possibly due to mass transfer limitations attributable to higher electrolyte viscosity. Thereby, the nature of the electrolyte and its relative composition play a significant role in the product distribution of the CO$_2$ reduction reaction.

The proposed methodology was brought one step forward into the scaling-up process and the validation of the electrochemical conversion in a semi-continuous system using an flow reactor was achieved for formic acid and for CO. The highest Faradaic efficiency towards CO (ca. 45 %) was achieved at -1.6 V vs Ag/AgCl with a current density of ca. 10 mA/cm$^2$.

This study presents a positive perspective in the implementation of the CCU technology by integrating CO$_2$ capture and conversion processes towards added value chemicals, such as formic acid or carbon monoxide.

Experimental

A three-electrode electrochemical H-cell and modular microflow cell (ElectroCell) were used to perform the electrochemical conversion of CO$_2$ for batch and flow experiments, respectively. The H-cell consisted of two compartments, while the flow cell had one extra compartment behind the cathode plate for heating purposes.

When working in the H-cell, the working electrode was a Pb coil (10 cm$^2$, Alfa Aesar, 99.9%) and the counter electrode was Pt coil (30 cm$^2$, Alfa Aesar, 99.9%). When working in the continuous flow cell, the working electrode was Pb foil (10 cm$^2$, Alfa Aesar, 99.9 %) for formic acid production and Au foil (10 cm$^2$, Alfa Aesar, 99.9%) for CO formation. The counter electrode was a platinized Titanium plate (10 cm$^2$, ElectroCell). The reference electrode used in both cells was a leak-free Ag/AgCl electrode (Innovative
The anode and cathode compartments in both cells were separated by pre-treated cation exchange membrane (Nafion-117). Prior to every experiment, the working and counter electrode were treated. Pb was treated electrochemically in a 0.5 M aqueous H$_2$SO$_4$ by applying -1.8V vs Pt as counter electrode for 500 s. The Pt coil was flame annealed, followed by quenching in Milli-Q water. Au foil was mechanically polished with alumina slurry, followed by sonication to remove trace alumina particles. All the glassware and cell components were rinsed with acetone and dried before using.

The anolyte consisted of a 0.5 M aqueous H$_2$SO$_4$ solution and the catholyte consisted of different concentrations (0, 0.5, 1, 2 and 3 M) of AMP and 0.7 M tetraethylammonium chloride (TEAC) in PC. A stock solution of 3 M AMP and 0.7 M TEAC in PC loaded with CO$_2$ was prepared in bulk and later diluted to the desired concentration. The stock solution was loaded with CO$_2$ at 15 °C for 2 hours with a CO$_2$ flow rate of 210 ml/min, and was stored at 5 °C. Prior to every H-cell electrolysis experiment, 40 min of N$_2$ purging at 15 °C was performed to remove all non-complexed, dissolved CO$_2$ from the catholyte solution. No extra CO$_2$ was fed during electrolysis. The heating of the electrolyte to the desired temperature was started at the same time as the chronoamperometry. In continuous-flow experiments, the vessel containing the CO$_2$ loaded catholyte was heated to 60 °C before starting chronoamperometry, to achieve a monophasic system, and avoid blockages in the recirculation pump. The measurements were carried in potentiostatic mode, applying a constant cathode potential of -2.5 V for experiments carried out on Pb electrodes and different potentials (-1.4, -1.6, -1.8 and -2 V vs Ag/AgCl) for experiments on Au electrodes. The potentials were controlled by an Autolab potentiostat (PGSTAT20).

The liquid products obtained during the reduction of CO$_2$ were collected every 30 minutes and analyzed using an Agilent High Performance Liquid Chromatograph (HPLC) system (1260-Infinity with and Amminex HPX-87H column and RID detector).

The gaseous products were analyzed using an Interscience gas chromatography (GC) system (Trace GC with a Supelco carboxen 1010 PLOT column and FID detector). CO$_2$ loading of the catholyte solution was measured prior to and during operation by the barium carbonate (BaCO$_3$) precipitation method as described by Li et. al.$^{42}$ and Santos et. al.$^{43}$ 1 ml of unfiltered catholyte solution was diluted with 10 ml of Milli-Q water to dissolve any solids, then 10 ml of 1 M BaCl$_2$ was added to form BaCO$_3$, which precipitates. This slurry was then titrated with 0.1 M HCl until the white precipitate disappeared completely.

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**Competing interests**
The authors declare no competing financial interest.

**Data availability**
The data that support the plots within this paper and other findings of this study are available from the corresponding author on reasonable request.

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