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**Capture and Electrochemical Conversion of  
CO<sub>2</sub> to Syngas with a Sustainable Ionic Liquid**



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## Riassunto

### A. Introduzione

La società moderna è fondata sull'utilizzo dei combustibili fossili, questo aspetto porta a incrementare la concentrazione di CO<sub>2</sub> in atmosfera con il conseguente innalzamento della temperatura. L'anidride carbonica è considerata il maggior responsabile dell'aumento termico globale (Figura 1.1 del corpo tesi) [1]. Il problema dell'aumento delle emissioni di CO<sub>2</sub> è stato affrontato da diversi fronti, una possibile e interessante soluzione è l'elettro-riduzione catalitica di CO<sub>2</sub> in CO. L'elettrocatalisi permette la conversione di CO<sub>2</sub> in prodotti come il metanolo, il monossido di carbonio, l'acido formico. Per questo obiettivo è necessaria la cattura del biossido di carbonio dall'atmosfera. Le sostanze che hanno la capacità di assorbire CO<sub>2</sub>, come le soluzioni amminiche, non sono ecologicamente compatibili con l'ambiente. Perciò in questo lavoro di tesi si è pensato di sostituire le soluzioni amminiche, con delle soluzioni innovative e biodegradabili: i liquidi ionici [2, 3].

Alcuni liquidi ionici sono stati utilizzati come elettrolita nella riduzione di CO<sub>2</sub> in soluzioni acquose. Queste sostanze presentano delle particolari e interessanti proprietà:

- Alta stabilità termica;
- Bassa pressione di vapore;
- Apprezzabile conducibilità ionica;
- Stabilità elettrochimica.

Sono evidenti i presupposti per utilizzare ILs nella separazione delle CO<sub>2</sub>.

Le soluzioni amminiche, ad esempio MEA, sono state utilizzate in passato per la loro capacità di assorbire la CO<sub>2</sub>. Le suddette soluzioni organiche presentano degli svantaggi che ne limita l'utilizzo nei processi industriali, quali la corrosione dei tubi, la degradazione irreversibile del materiale assorbente e l'alto consumo energetico. Inoltre c'è da considerare che oggi, fortunatamente, è necessario valutare la compatibilità ambientale delle sostanze utilizzate nei processi: un altro svantaggio per le soluzioni amminiche. Per superare queste problematiche hanno avuto grande attenzione dagli istituti di ricerca i liquidi ionici funzionali per la cattura di CO<sub>2</sub> [1, 4].

Le interazioni che si formano tra la stabile molecola di diossido di carbonio e la molecola di liquido ionico sono principalmente composti da forze elettrostatiche, forze di Van der Waals e legami a idrogeno: è presente un assorbimento fisico [5].

La solubilità di CO<sub>2</sub> nella molecola di liquido ionico è influenzata dalla struttura di anione e catione. La crescita della lunghezza della catena alchilica nel catione, aumenta la solubilità. Tuttavia, è sempre maggiore l'effetto dell'anione rispetto al catione sulla solubilità di CO<sub>2</sub>, che per questo motivo è più studiato [5, 6].

La ricerca di un'alta capacità di assorbimento ha portato ad introdurre degli opportuni gruppi funzionali nella molecola del liquido ionico, con lo scopo di far avvenire la reazione desiderata, viene incrementata la capacità di assorbimento chimico. In primis è stato aggiunto un gruppo

amminico per rendere funzionale la molecola di liquido ionico [6]: 1-butile-3-propilamminimidazolo tetrafluoroborato. Inserendo i gruppi funzionali di ammine nella struttura della molecola del IL si ha una reattività specifica. I gruppi amminici assorbono la CO<sub>2</sub> in due modi diversi: formazione di carbammato e formazione di carbonato. La reazione di ammine primarie e secondarie consiste in due steps:

- Formazione dello switterione;
- Depronatazione dello switterione.

Il primo step è limitante. Le ammine terziarie formano un carbammato instabile.

Sono stati sviluppati dei liquidi ionici funzionali non amminici come le super basi derivanti da ILs protici o ILs con gruppi fenolici che presentano sul catione dei siti multi attivi [1, 7].

La solubilità di CO<sub>2</sub> è richiesta per abbassare i costi del processo, ed è influenzata dalla grandezza sterica dell'anione. Un anione fluorinato incrementa la solubilità, si sostituiscono gli atomi di idrogeno con il fluoro che è più elettronegativo. Si forma una debole base di Lewis che interagisce più facilmente con il gruppo carbonile contenuto nella molecola di CO<sub>2</sub>. Si ha la formazione di un legame polare C-F. Il comportamento del fluoro è interessante e promettente e sono studiati altri composti che lo contengono, per capire le interazioni che si formano.

Un altro modo per incrementare la solubilità è quello di utilizzare come catione la molecola di imidazolo o piridina, che hanno simili performance. La piridina è più economica e più biodegradabile. Il gruppo carbonile nell'anione e/o nel catione aumenta la solubilità. Inoltre, la molecola di CO<sub>2</sub> può essere considerata simultaneamente un acido di Lewis e una base di Lewis. In letteratura si trovano numerosi esempi di tali funzionalizzazioni.

In questa tesi ci siamo focalizzati sui liquidi ionici funzionalizzati con gli amminoacidi (AAILs). La molecola di amminoacido ha un gruppo carbossilico residuo e un gruppo amminico (Figure 1.2). Gli amminoacidi si presentano con potenziali benefici: bassa pressione di vapore e bassa tossicità, tra i più importanti. Tuttavia, presentano un'alta viscosità. La caratteristica principale delle molecole di un amminoacido è il carbonio chirale. Si è visto che ILs funzionalizzati con amminoacidi hanno un'elevata capacità di assorbimento. Abbiamo testato una soluzione di colina glicina (ChoGly) e abbiamo verificato l'assorbimento al variare di fattori fisici.

I liquidi ionici sono utilizzati come elettrolita nella riduzione di CO<sub>2</sub> in CO, in un sistema elettrocatalitico. I catalizzatori più noti per la riduzione di anidride carbonica in CO sono Ag, Au, Cu e Zn. La molecola di CO<sub>2</sub> è molto stabile e lineare, richiede un'alta quantità di energia per essere ridotta elettrochimicamente, la cui reazione è un processo difficile, non spontaneo e lento. La riduzione di CO<sub>2</sub> può avvenire verso altri prodotti come acido acetico e metanolo.

Il sistema elettrochimico per la riduzione di CO<sub>2</sub> è composto da un catodo, elettrodo che catalizza la reazione e da un anodo. Gli elettrodi possono essere presenti nel medesimo bagno elettrolitico o essere separati in scompartimenti specifici da una membrana protonica. La separazione delle camere è un'ottimizzazione per entrambe le reazioni, tuttavia questi sistemi, ad oggi, non raggiungono un'efficienza tale da garantire uno sviluppo commerciale. La molecola di CO<sub>2</sub> è stabile termodinamicamente, quindi è sfavorito il primo step per la riduzione.

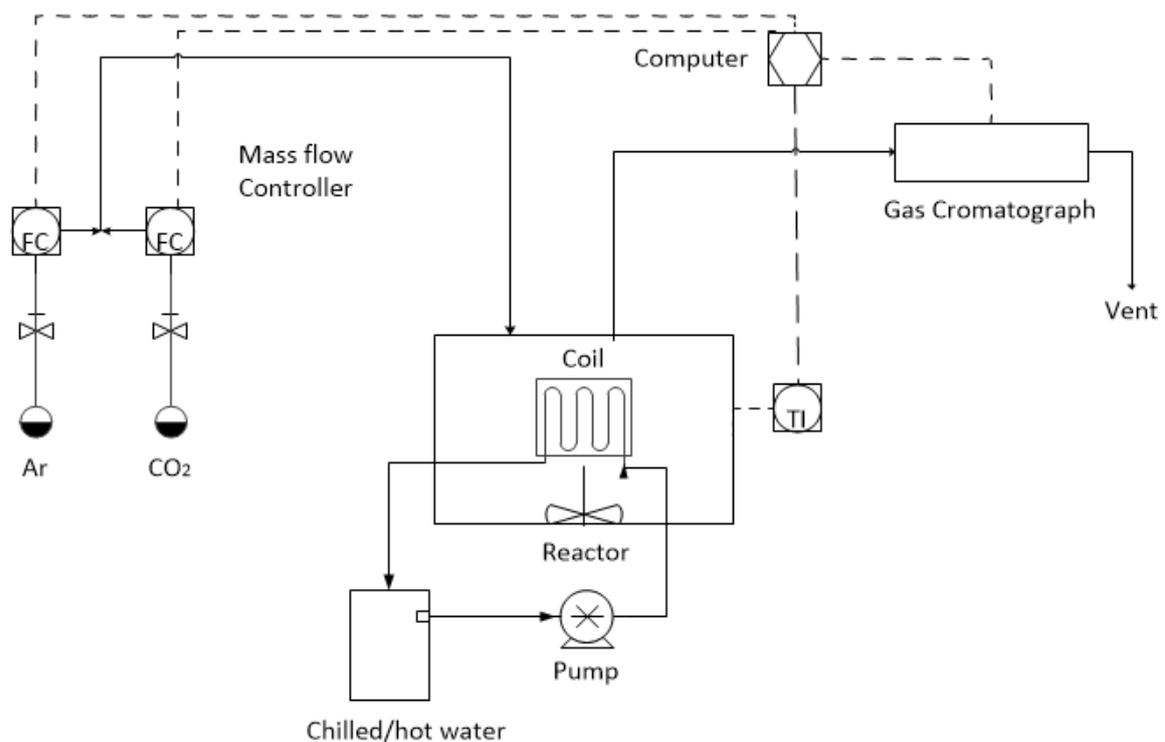
Oltre a materiali catalitici innovativi, o nuove strutture di materiali catalitici, come i nanotubi di titanio o nanoparticelle di argento, si testano diverse soluzioni da utilizzare come elettrolita.

Il ChoGly utilizzato per i nostri esperimenti, è stato sintetizzato e caratterizzato nel centro CFST@Polito del Istituto Italiano di Tecnologia, e si presenta con una densità elevata (1122 g/l). ChoGly è un AAIL utilizzato a bassa pressione (1atm) per migliorare la performance dell'assorbimento di CO<sub>2</sub>. In letteratura non ci sono studi con l'utilizzo del ChoGly come elettrolita, nella riduzione catalitica di biossido di carbonio in monossido di carbonio.[3, 8]

### B. Test di assorbimento

Si è studiata la capacità di assorbimento di CO<sub>2</sub> in una soluzione di ChoGly per verificare che l'utilizzo del liquido ionico favorisca il processo di cattura del biossido di carbonio nel liquido.

Gli esperimenti sono stati effettuati con un apposito setup, prestatato schematicamente dalla Figura 1.



**Figura 1:** Schema illustrativo del setup di assorbimento di CO<sub>2</sub>

Il setup consiste in:

- Reattore;
- Pompa peristaltica collegata a una serpentina contenuta nel reattore;
- Gas Cromatografo (GC);
- Due Controllori di portata ;

Il volume di soluzione contenuta nel reattore è pari a 40 ml. Prima di iniziare l'esperimento, sono necessari dei passaggi preliminari. Viene prima mandata una portata di Ar per togliere l'aria contenuta nel reattore e verificare che non ci siano perdite: quando la concentrazione di azoto letta dal GC è vicina a zero è possibile iniziare l'esperimento. Contemporaneamente viene portato il reattore alla temperatura desiderata, mantenuta costante grazie al ricircolo costante di acqua di raffreddamento con una pompa peristaltica. A questo punto viene fatta gorgogliare una miscela di CO<sub>2</sub> e Ar nota, quindi, passato il tempo di assorbimento, si leggerà dal GC la concentrazione inviata al reattore. Tale concentrazione è letta in continuo, ma con un tempo di ritardo dato dai tubi che collegano il reattore e il GC. Il processo di assorbimento di CO<sub>2</sub> è una reazione esotermica, quindi la temperatura tende ad aumentare per il calore rilasciato dalla reazione. La pompa peristaltica mantiene costante la temperatura allontanando il calore latente. Il processo di assorbimento della soluzione si può considerare terminato quando la concentrazione di CO<sub>2</sub> in ingresso è pari alla concentrazione in uscita. Con il volume pari a 40ml di acqua bidistillata, è stato svolto l'esperimento descritto per conoscere il ritardo del sistema e la seppur minima capacità di assorbimento di CO<sub>2</sub> in H<sub>2</sub>O. La capacità di assorbimento dell'acqua e il ritardo del sistema è stato valutato a diverse temperature (24 °C, 34 °C, 44 °C), in quanto la solubilità di un gas è influenzata da temperatura e pressione.

I valori di concentrazione (in ppm o %mol) sono determinati con un GC (Inficon, Micro GC Fusion Gas Analyzer). Dal bilancio di materia è possibile valutare la quantità di CO<sub>2</sub> assorbita dalla soluzione, conoscendo la concentrazione in entrata. Gli esperimenti con le soluzioni di liquido ionico, saranno valutati e purati dal ritardo dato dalla soluzione considerata come bianco, e si è calcolato il reale effetto di ChoGly nella soluzione. Il calcolo dell'integrale cumulativo della curva che illustra come varia la concentrazione in funzione del tempo, è accompagnato da un calcolo qualitativo. Si è misurato il peso della soluzione prima (soluzione fresca) e dopo il gorgogliamento di CO<sub>2</sub> e si è valutata la percentuale di assorbimento di CO<sub>2</sub>. Il calcolo qualitativo, seppur con un errore maggiore del calcolo quantitativo, ne conferma il trend.

Si è studiato l'effetto che il ChoGly ha sulle performance di assorbimento delle soluzioni variando i seguenti parametri:

- Concentrazione;
- Temperatura;
- Portata di gas;
- Solvente.

Con le soluzioni di acqua come solvente e ChoGly come soluto, al 10% (volume di ChoGly / volume di H<sub>2</sub>O), 20 %, 30 % e 40 % si sono svolti gli esperimenti di assorbimento di CO<sub>2</sub>. La temperatura si è mantenuta costante a 24°C e la portata del gas mandato nel reattore pari a 40 ml/min composta di 25 % di CO<sub>2</sub> in Ar.

Successivamente, con una soluzione al 20% (v/v) di ChoGly, con una portata di CO<sub>2</sub> nel reattore pari a 25 % della portata totale, si è studiato l'effetto della temperatura. Si è valutata la capacità di assorbimento a 24 °C, 34 °C e 44 °C.

Si è valutato l'effetto sul processo della portata di CO<sub>2</sub>. Per mantenere la stessa portata totale si è variata la % di CO<sub>2</sub> 13 %. Sono state valutate le differenze tra le soluzioni contenenti diverse concentrazioni di ChoGly.

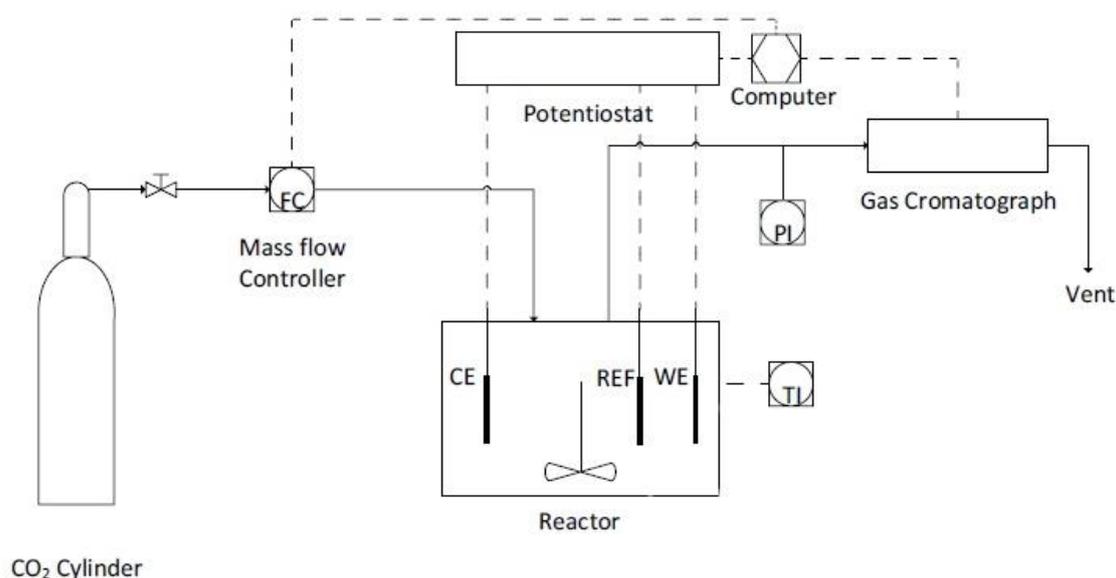
Infine si è considerato il solvente come variabile. L'acqua è stata sostituita da soluzioni acquose di KOH e KCl, formando le soluzioni che sono state testate a 24 °C, ognuna con il rispettivo bianco.

### C. Test di elettrocatalisi

Il setup utilizzato comprende:

- Reattore
- Potenziostato;
- Gas Cromatografo (GC);
- Controllore di portata;
- Elettrodo di Riferimento.

Il reattore è la cella elettrochimica dove avvengono le reazioni, è agitato magneticamente ed è collegato al potenziostato che applica il potenziale richiesto tra gli elettrodi. La differenza di potenziale è applicata tra il catalizzatore (WE), che è un foglio di argento (SIGMA-ALDRICH, silver foil, thickness 0.25 mm, 99.99 %) e l'elettrodo di riferimento (REF) (Radiometer Analytical, REF421 saturated calomel electrode). L'anodo è una spirale di platino (CE). Il GC preleva il gas dall'interno del reattore e indica la concentrazione dei prodotti. L'ingresso di CO<sub>2</sub> è regolato da un controllore di portata (Bronkhorst EL-FLOW model F-201CV). La portata di CO<sub>2</sub> è gorgogliata direttamente nella soluzione liquida e la dissoluzione del gas è favorita dall'agitazione magnetica.



**Figura 2:** Schema illustrativo del setup elettrocatalisi

Le due mezze reazioni che avvengono nella cella elettrochimica all'anodo e al catodo sono le seguenti (Equazione 1-Equazione 2):





La soluzione di KOH 2M è il nostro bianco, per vedere l'effetto reale di ChoGly in soluzione e sono state valutate le cronoamperometrie (CA) a tre differenti potenziali. Le analisi di CA indicano la corrente nel tempo, durano 90 minuti. Questa tecnica misura la resistenza tra l'elettrodo di riferimento e il catodo, che è il materiale che catalizza la reazione. I potenziali testati sono -1,3V, -1,4V e -1,5V e gli esperimenti sono stati svolti per tre elettroliti: il bianco, una soluzione di KOH 2M e ChoGly 0,8 M, una soluzione contenete solo il ChoGly 0,8M. Nelle tabelle 3.3 e 3.4 (corpo della tesi) si possono vedere i valori di pH e conduttività delle soluzioni utilizzate, nella soluzione fresca e dopo il gorgogliamento di CO<sub>2</sub>. Il biossido di carbonio è una sostanza notoriamente acida e il suo gorgogliamento acidifica la soluzione.

Si sono elaborati i dati ottenuti dal potenziostato e dal gas cromatografo. Il potenziostato, durante l'esperimento, fornisce dei dati con un intervallo di tempo molto inferiore rispetto al gas cromatografo, che necessita di 2,2 minuti per elaborare i dati. Quindi i dati del potenziostato possono essere definiti istantanei.

La superficie catalitica è pari a 2,4 cm<sup>2</sup>, la pressione e la temperatura sono quelle dell'ambiente.

Si riporta di seguito l'elaborazione dei dati.

La densità di corrente è pari al rapporto tra la corrente, valore dato dal potenziostato e l'area dell'elettrodo (Equazione 3).

$$j = \frac{I}{A} \quad (3)$$

dove:

$j$  [mA/m<sup>2</sup>] è la densità di corrente;

$I$  [mA] è la corrente elettrica;

$A$  [m<sup>2</sup>] è la superficie del catalizzatore.

Conoscendo la portata di gas entrante è possibile calcola la produzione di H<sub>2</sub> e CO come segue (Equazione 4- Equazione 5):

$$\dot{n}_{CO} = \frac{y_{CO} \cdot \dot{V} \cdot P}{R \cdot T \cdot A} \quad (4)$$

$$\dot{n}_{H2} = \frac{y_{H2} \cdot \dot{V} \cdot P}{R \cdot T \cdot A} \quad (5)$$

Dove:

$\dot{n}$  ( $\frac{mol}{s \cdot m^2}$ ) è la produzione di H<sub>2</sub> e CO;

$\dot{V}$  ( $\frac{m^3}{s}$ ) è la portata volumetrica del gas;

$P$  (Pa) è la pressione;

$R \left( \frac{m^3 Pa}{mol K} \right)$  è la costante dei gas;

$T (K)$  è la temperatura;

$A (m^2)$  è la superficie dell'elettrodo.

Si calcola infine l'Efficienza Faradica (Equazione 6)

$$FE_{CO} = \frac{\dot{n}_{CO} \cdot Z_{CO} \cdot F}{j} \cdot 100 \quad (6)$$

$$FE_{H2} = \frac{\dot{n}_{H2} \cdot Z_{H2} \cdot F}{j} \cdot 100 \quad (7)$$

Dove:

$\dot{n}_{CO}$  and  $\dot{n}_{H2} \left( \frac{mol}{s m^2} \right)$  sono le produzioni di CO e H<sub>2</sub>;

$Z_{CO}$  and  $Z_{H2} \left( \frac{mol e^-}{mol} \right)$  sono gli elettroni di cui la reazione necessita per formare rispettivamente una molecola di CO e H<sub>2</sub>;

$F \left( \frac{C}{mol e^-} \right)$  è la costante di Faraday;

$j \left( \frac{A}{m^2} \right)$  è la densità di corrente.

#### *D. Risultati e discussione*

##### *Risultati dai test di Assorbimento*

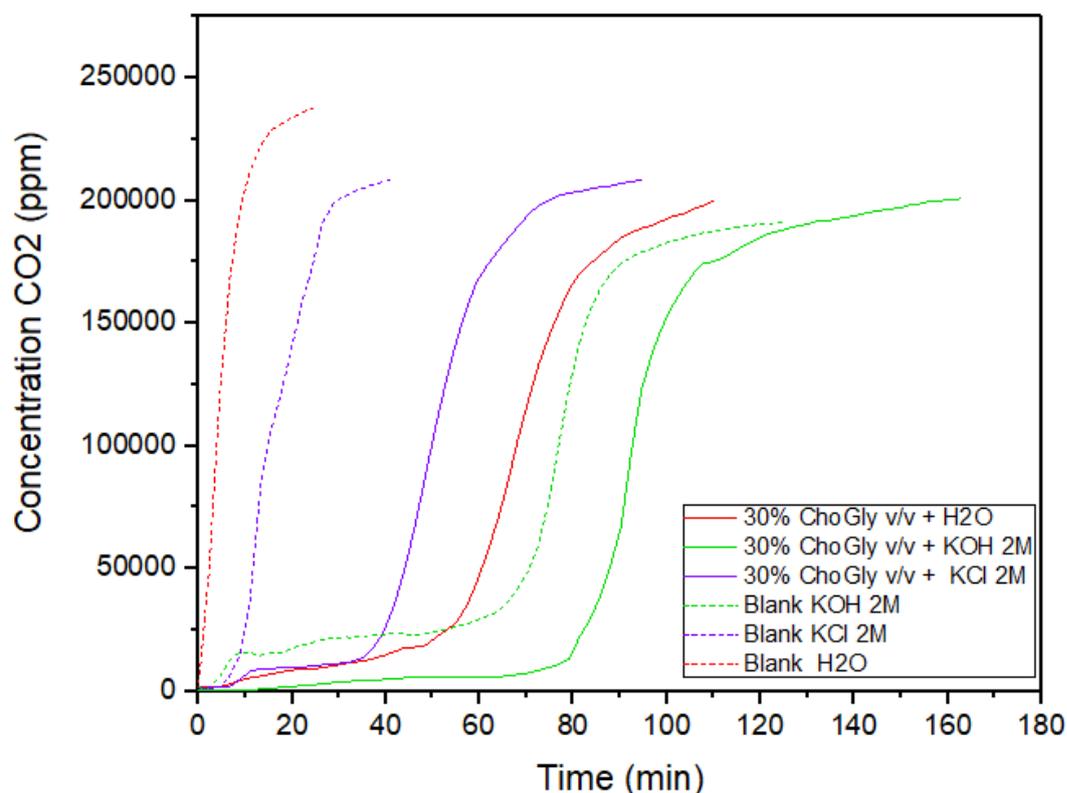
I risultati ottenuti dai test di assorbimento sono stati soddisfacenti. La soluzione contenente ChoGly assorbe una quantità maggiore di CO<sub>2</sub> rispetto alle soluzioni dove il liquido ionico è assente. Si è visto che incrementando la concentrazione del liquido ionico la cattura della quantità di CO<sub>2</sub> aumenta. Dalla Figura 5.1 (corpo tesi) è visibile che il tempo necessario alla saturazione della soluzione aumenta con la concentrazione, in quanto aumenta la capacità di assorbimento. Bisogna considerare che aumentare la concentrazione del liquido ionico comporta un incremento della viscosità della soluzione e ovviamente dei costi.

Dal calcolo dell'area sottesa alla curva di assorbimento si è potuta calcolare la massa di CO<sub>2</sub> assorbita dalla soluzione e il rapporto tra i mg di CO<sub>2</sub> catturata e la massa del liquido ionico. Tutti i calcoli sono epurati dal ritardo del sistema e dall'assorbimento dell'acqua (Tabella 5.1 corpo tesi). Il calcolo quantitativo conferma quella qualitativo i cui risultati sono riportati nella Tabella 5.2 (corpo tesi) con l'aumento di assorbimento con l'incremento di ChoGly in soluzione.

I risultati ottenuti dai test, a 24°C, 34°C e 44°C, indicano una diminuzione della capacità di assorbimento con l'aumento di temperatura. La reazione di assorbimento, essendo esotermica, è favorita a temperatura ambiente (24°C). la differenza tra le curve a 34°C e 44°C è minima, quindi aumentando ancora la temperatura ci aspettiamo il medesimo assorbimento. Dalle tabelle 5.3 e 5.4 si possono vedere i valori numerici dalla quantità di CO<sub>2</sub> assorbita per una soluzione 20% ChoGly in acqua (v/v) calcolati rispettivamente con il metodo quantitativo e qualitativo.

La variazione di portata di CO<sub>2</sub> in ingresso nel reattore porta l'aumento del tempo necessario per la saturazione della soluzione. Si riportano le curve per le soluzioni al 10% e 20% di ChoGly (v/v) con il 13% e 25% di CO<sub>2</sub> sulla portata totale di gas entrante (Figura 5.5 corpo della tesi).

Infine si è valutato l'effetto dell'interazione tra ChoGly e solvente. Sono state valutate le soluzioni di acqua, KOH 2M e KCl 2M. La Figura 3 mostra le curve di assorbimento ottenute. L'assorbimento maggiore si ha con la soluzione di idrossido di potassio 2M con ChoGly, ma l'effetto del ChoGly è basso, visto che la soluzione di KOH pura ha una capacità di assorbimento elevata. Considerando H<sub>2</sub>O pura, la sua capacità di assorbire CO<sub>2</sub> è la più bassa, ma aggiungendo il 30 % v/v di ChoGly raggiunge assorbimenti alti. Le performance del ChoGly sono migliori quando la soluzione di partenza non eccelle nell'assorbimento, massimizzando così il suo effetto. La soluzione di KCl ha un comportamento intermedio e la posizione delle sue curve, con e senza ChoGly, conferma quanto detto.



**Figura 3:** Assorbimento di CO<sub>2</sub> in differenti soluzioni

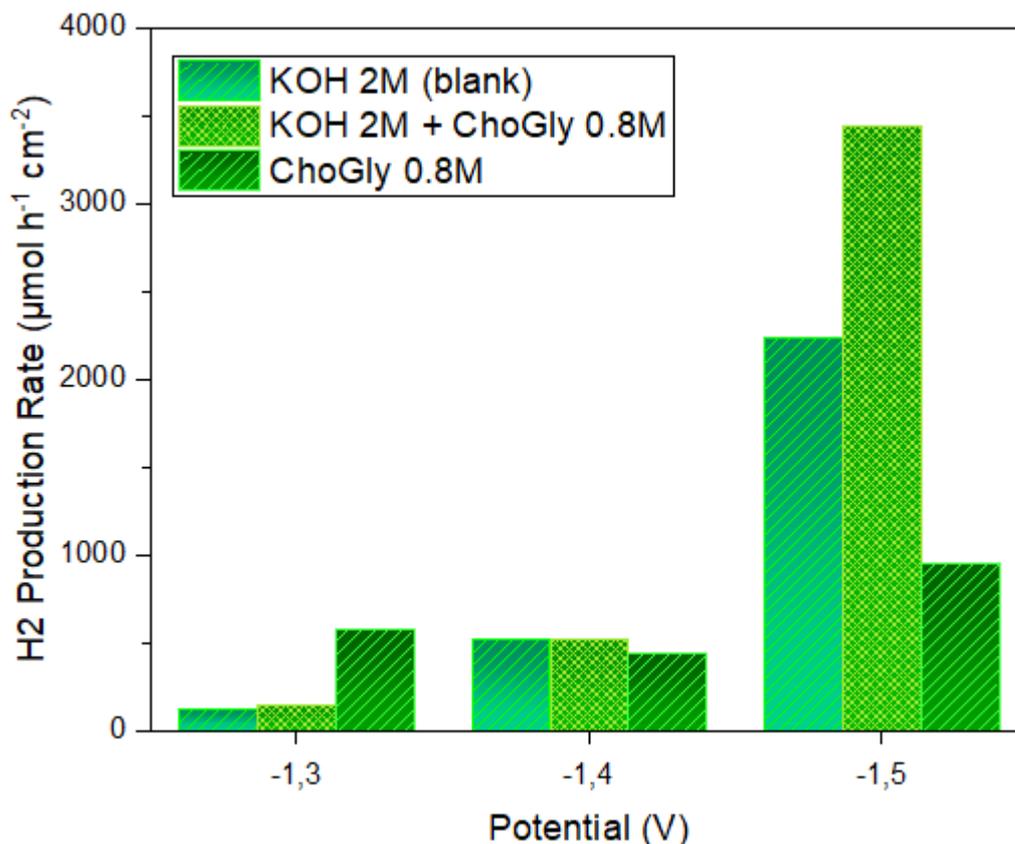
I calcoli della cinetica di assorbimento sono epurati dal rispettivo solvente e confermano quanto ipotizzato. I valori numerici di assorbimento sono riportati dalle tabelle 5.6 e 5.7 (corpo tesi) e confermano la nostra assunzione.

#### *Risultati dai test di elettrocatalisi*

I risultati ottenuti dai test di elettrocatalisi, ci si aspettava che la soluzione, avendo assorbito una maggiore quantità di CO<sub>2</sub>, fosse capace di produrre una quantità di CO maggiore. Dai test svolti si vede che questa ipotesi è stata smentita.

Nella Figura 4 è riportata la produzione di H<sub>2</sub> ottenuta per i tre potenziali considerati, delle diverse soluzioni esaminate. Vediamo che l'effetto del ChoGly è quello di aumentare la

produzione di idrogeno, visibile a occhio nudo nel reattore durante l'esperimento. A -1.3V produce una maggior quantità di idrogeno la soluzione contenente solo il ChoGly 0.8 M mentre a -1.4V le produzioni sono paragonabili. A-1.5V è visibile un effetto controverso del ChoGly: la massima produzione di H<sub>2</sub> si ha per la soluzione KOH 2M e ChoGly 0.8M e la soluzione che produce meno H<sub>2</sub> è quella contenente unicamente il ChoGly. Le interazioni che si formano tra KOH e ChoGly sono tali da favorire la formazione di idrogeno. Questo interessante comportamento andrebbe investigato per comprendere il tipo di legami che interagiscono tra le molecole di ChoGly e KOH e quali sono i fattori che favoriscono tali interazioni.



**Figure 4:** *Produzione di H<sub>2</sub> a differenti potenziali con diversi elettroliti*

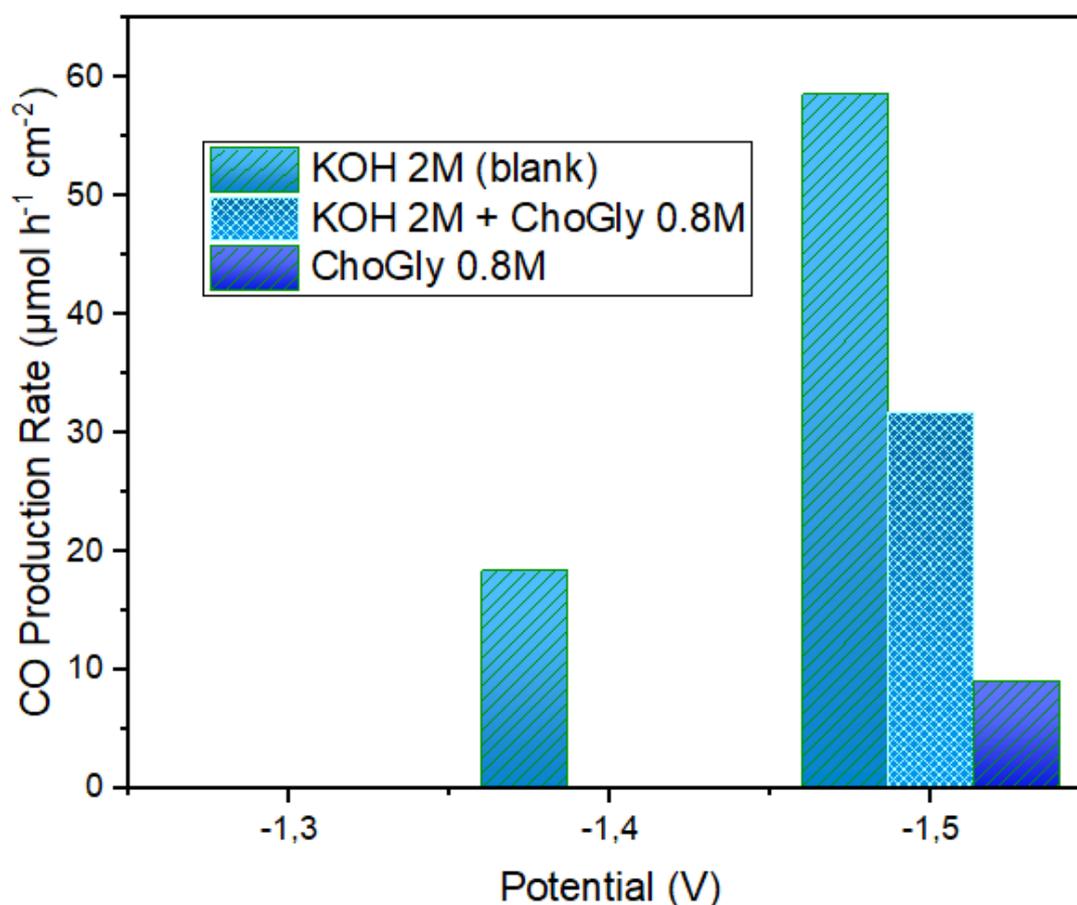
Nella Figura 5 si vede che il bianco considerato, la soluzione di KOH 2M puro, ha prodotto una maggior quantità di CO rispetto alle soluzioni contenenti il ChoGly. Con un potenziale pare a -1.3V non si verifica la produzione di monossido di carbonio. Si ha produzione di CO sono nella soluzione di KOH 2M a -1.4 V. Si verifica la produzione di monossido di carbonio per tutte le soluzioni esaminate a -1.5V, ma in quantità differenti. Il liquido ionico esaminato, evidentemente, inibisce la formazione del radicale CO<sub>2</sub><sup>-</sup> che è il rate determining step del processo di riduzione elettrochimica della CO<sub>2</sub>, così sfavorendo la produzione di CO.

Si è calcolata l'efficienza Faradica che è riportata nella Tabella 1.

**Tabella 1:** *Efficienza di Faraday di CO*

Solution	-1.3 V	-1.4 V	-1.5 V
KOH 2M	-	3.7	8.52
KOH 2M + ChoGly 0,8M	-	-	1.29
ChoGly 0,8M	-	-	1.50

I risultati dell'efficienza di Faraday per la produzione di CO confermano le supposizioni nate dalla visione delle figure riguardanti la produzione di monossido di carbonio.



**Figura 5:** *Produzione di CO a differenti potenziali con diversi elettroliti*

### *E. Conclusione*

Il problema del riscaldamento globale dovuto a un incremento delle emissioni di  $\text{CO}_2$  ha portato la ricerca scientifica ad ambire alla cattura dall'atmosfera e alla riduzione di  $\text{CO}_2$ . Lo studio della conversione elettrochimica di  $\text{CO}_2$  in CO si estende dai catalizzatori utilizzati, al reattore ottimale, all'elettrolita. Il mio studio si è focalizzato sugli elettroliti e tra i possibili candidati i liquidi ionici spiccano per le loro interessanti proprietà. Il principale scopo dalla tesi è che il processo di conversione utilizzi delle sostanze compatibili con l'ambiente e i liquidi ionici si

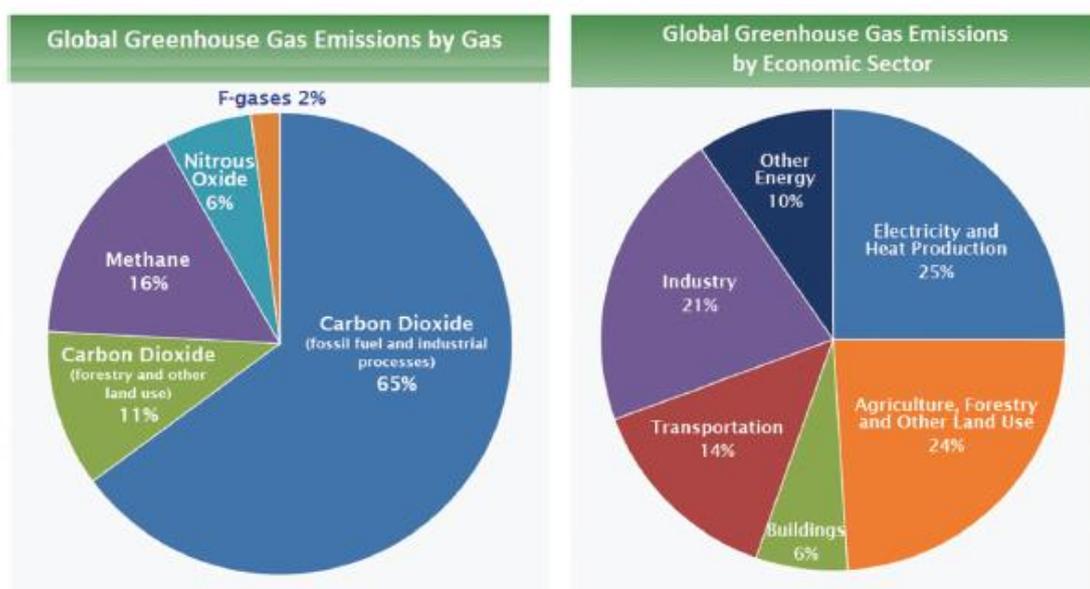
propongono come sostituti delle meno sostenibili soluzioni amminiche. Si è testato un AAIL, il ChoGly. Nelle prove di assorbimento, il ChoGly ha dato risultati soddisfacenti. Nelle prove di elettrocatalisi, che per un AAIL non hanno riscontri in letteratura, si è compreso che le interazioni che il ChoGly è in grado di formare, devono essere ancora investigate e studiate, come anche i fattori che le influenzano. È interessante comprendere il perché il ChoGly favorisce la reazione per la produzione di idrogeno e sfavorisca il processo per la produzione di monossido di carbonio. Inoltre sarebbe interessante confrontare i dati ottenuti con il ChoGly con un altro liquido ionico della stessa specie, ad esempio il ChoAla, a parità di condizioni.



# 1. Introduction

## 1.1 The objective of this work

The global warming is an important problem which has been addressed in many ways. The most important reason for climate change is the increase in the concentration of greenhouse gases in the atmosphere [1]. Carbon dioxide is considered the main responsible of global warming, human activities increased CO<sub>2</sub> emissions in the atmosphere, although this emission exists in natural carbon earth cycle. The modern society is irremediably founded by carbon fuels, and its economy is based by the combustion of fossil fuel. In Fig. 1.1 it is shown that about 65% of the global greenhouse gas (GHG) emission is constituted by CO<sub>2</sub>. Carbon dioxide derived from the use of the fossil fuels and industrial process. [2]



**Figure 1.1:** Global greenhouse gas emissions by human activities and classification by economic sector's production. Reproduced from Ref [2] with permission of The Royal Society of Chemistry.

Simultaneous implementation of multiple approaches has been proposed to mitigate the negative effect of CO<sub>2</sub> emissions [3]. Due to this problem, many researchers are investigating an interesting possible solution, that is, is the conversion of CO<sub>2</sub> by its electrochemical reduction to other high-added value compounds. The electrochemistry and the research could provide an opportunity to reduce the global warming, because the electrocatalytic reduction of CO<sub>2</sub> is a promising way to reuse this greenhouse gas for the production of fuels or chemicals like formic acid, CO, methanol and other hydrocarbons. For converting CO<sub>2</sub> from the atmosphere is the first step that have be faced. U to now, amine solutions are used for that purpose, but this method is not eco-friendly. During the last decades, ionic liquids (ILs) have received great attention as potential alternatives to common ammine solutions such as mono-ethanolamine, MEA. Ionic liquids are tuneable and promising due to their great chemical and physical CO<sub>2</sub> absorption, however they have a high viscosity. The large use of cations and

anions make these ionic liquids more versatile. Using various combinations of ions, it should be possible to develop more advanced electrocatalytic systems for commercial use[4].

The purpose of this thesis is to show the use of ionic liquids in CO<sub>2</sub> reduction and to understand the mechanism of the electrocatalysis in the presence of those compounds. We investigate the common principles that govern the catalysis for different electrochemical reactions, with different ILs as electrolyte. We have tested in laboratory a novel ionic liquid composed by Choline Glycine in order to verify its potential applications as electrolyte for the CO<sub>2</sub> capture and conversion in an electrochemical system for the production of Syngas (a mixture of H<sub>2</sub> and CO<sub>2</sub>).

The novel liquid has been synthesized in the chemical laboratory at the CFST@Polito center of the Italian Institute of Technologies (IIT) in Turin and the experimental tests of both absorption and electrochemical reduction of CO<sub>2</sub> have been done at Politecnico di Torino in the Solar Fuels Lab (CREST group).

## *1.2 Ionic liquids ILs*

As potential green solvent, ionic liquids (ILs) are different than common organic solvents. ILs consist of anion and cation, which present unique properties. The influence of cation and anion can improve the capture of CO<sub>2</sub>. There is a large choice of ions, that have been investigated. ILs present interesting thermodynamic properties as a low melting point, high thermal stability, negligible vapor pressure and designable physicochemical characteristics [1, 9].

They belong to a class of organic salts, with lattice energies lower than those common in inorganic salts. They are affected by their asymmetric structure. ILs are salts that can exist as liquid at room temperature, they have exhibited outstanding properties such as wide electrochemical window, high electrical conductivity, adjustable acidity, high dissolving capacity for inorganic and organic compounds and can be recycled [5].

In the recent past, the CO<sub>2</sub> capture happened with traditional ammine solutions such as MEA. This method brings many problems such as the pipeline corrosion, the high energy consumption and the absorbent degradation. The industrial application of this method is limited. Furthermore, nowadays we try to find the sustainable development. To solve these disadvantages, ILs have been developed as novel CO<sub>2</sub> absorbents.

There are different works in literature that aim to investigate the absorption of CO<sub>2</sub> with the use of machine learning based models to establish structure-property relationships between molecular structures of cations and anions[10].

To solve the problem, many new absorbents are being developed: functionalized ILs. The physical interactions between ILs and the molecular of carbon dioxide are mainly composed of electrostatic, Van der Waals and hydrogen-bonding forces [1].

To understand the mechanism the concept of free volume has been introduced. Fractional free volume consists in the ratio of empty space to the space occupied in a material. If free volume increases, there is more space for gas molecules. In fact the CO<sub>2</sub> solubility is usually proportional to the free volume [6]. Owing to coulombic interaction between the ions of ILs, ILs present a

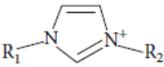
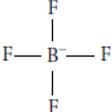
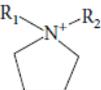
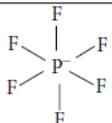
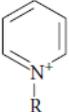
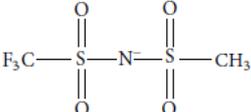
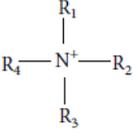
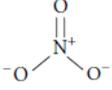
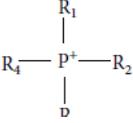
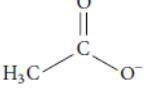
small volume expansion. The rigid network of cations and anions in ILs potentially includes a large amount free volume; these free spaces can be occupied by the CO<sub>2</sub> molecules.

### 1.2.1 CO<sub>2</sub> solubility in ILs

A high CO<sub>2</sub> solubility is needed to achieve a cost-effective process. It has been compared physical and chemical absorption using ILs. The chemical absorption required more energy.

Upon the physical absorption of carbon dioxide using ILs, the size of anion is the main factor influenced the CO<sub>2</sub> solubility, as showed in Table 1.1. In fact, the presence of the aromatic ring or other bulky molecular structure influenced carbon dioxide solubility. This could be inferred on the basis of the observation of the solubility measurements and results from molecular dynamics simulation. The structure of cation of IL also influences the CO<sub>2</sub> solubility[1].

**Table 1.1:** Common cation and anion in ILs. Reproduced from the Ref. [11]

Imidazolium		Tetrafluoroborate	
Pyrrolidinium		Hexafluoroborate	
Pyridinium		Bis(trifluorophosphate)imide	
Quaternary Ammonium		Nitrate	
Tetra Alkyl Phosphonium		Acetate	

The characteristics are particularly advantageous when applying ILs as solvent for carbon dioxide capture in comparison to current aqueous amine technology. Low energy is required for the CO<sub>2</sub> capture, due to their physical absorption mechanism. The tuneable design of ILs offers many options, in the sense that the anions and cations can be manipulate for create IL for a carbon dioxide capture [11]. The capacity for CO<sub>2</sub> solubility in ILs is originated by the asymmetric design and structure of molecules. The solubility of CO<sub>2</sub> is influenced by the pressure and temperature. In general, when the pressure increased, the solubility grows. The temperature increases causes a decrease in the solubility [1, 12].

### 1.2.2 Anion and cation effects

Interesting is the influence of the ions that constitute the ionic liquid. It has been observed that the anion(s) has a greater effect for the carbon dioxide solubility than cation(s) [11, 12]. About the anion, results that the fluorinate anion increased the CO<sub>2</sub> solubility. The results of some studies revealed that ILs with fluorinate anions increase more the CO<sub>2</sub> solubility than non-fluorinate anions. The reason of this has been observed in the presence of CO<sub>2</sub>-philicity group, as example S=O group. It was found that S=O group increased the CO<sub>2</sub>-philicity of molecules because there are the Lewis interactions between CO<sub>2</sub> molecules and S=O group [13].

To improve the performance of ionic liquids, one method is to introduce CO<sub>2</sub>-philic groups in the cation or/and in the anion. The literature survey indicates that the presence of functional groups, such as amines group, fluorine atoms, and carbonyl groups, that increased the carbon dioxide absorption. [1, 13, 14].

The functionalized ionic liquids are targeted to improve the performance of a common ILs in given application by means of changes on the constitutive ion structure[14]. The functionalized ILs are the task-specific solvents for the absorption of CO<sub>2</sub>. In this context, it is a great importance to investigate the reaction that allows CO<sub>2</sub>-philic to capture CO<sub>2</sub> and the relationship with the molecular structure. There are also, different captures using primary, secondary or tertiary amines.

The CO<sub>2</sub>-philicity of fluorinated molecules is due to a higher electronegativity of fluorine atoms than hydrogen atoms, it is preferred to carry out a stepwise fluorination of hydrocarbons leading to weak Lewis base units. The weak Lewis units can interact with the carbon atoms of CO<sub>2</sub> owing to the generation of polar C-F bond [5, 15]. In the molecules that are partially fluorinated compounds, the hydrogen is electron deficient and that can attractive the oxygen with the bond C-H...O [15, 16]. There is an excellent reversibility due to the presence of the enhanced Lewis and cooperative hydrogen interactions. [12]

Carbonyl groups are traditional used to improve the CO<sub>2</sub> solubility. The interaction between carbon dioxide and a carbonyl group indicated that CO<sub>2</sub> can simultaneously act as Lewis acid and Lewis base; that is the carbon atoms of CO<sub>2</sub> interacts as Lewis acid with the carbonyl of the group. One oxygen of CO<sub>2</sub> can interact as Lewis base. In literature we can find that the CO<sub>2</sub>-philicity of carbonyl function is influenced by fluorination [17].

The introduction of amine groups in the cation or anion presents the easier method among the different strategies developed for the enhancement of CO<sub>2</sub> capacity [18]. This change of structure is investigated in many works. Amino functional groups absorbed CO<sub>2</sub> through two different ways: formation of carbamate and formation of carbonate, which have a reaction with carbon dioxide.

The reaction of primary and secondary amines with CO<sub>2</sub> consists in two steps:

- formation of zwitterion
- the base-catalyzed deprotonation of the zwitterion [18-20].

The formation of zwitterion carbamate is considered a barrier. The primary and secondary amines form a stable carbamate. The carbamate formation required a lot of energy to break the bond and regenerate the absorbent. The first step of the reaction is bimolecular, and the product

of the first reaction step is a zwitterion. The zwitterionic carbamate,  $R-^+NH_2-COO^-$ , undergoes proton abstraction by the Lewis base. The newly formed carbamate or an available amine group can abstract the proton back from  $BH^+$ , where B is considered Lewis base. The mechanism is usually referred to as the zwitterion mechanism. In cases where an overall second-order reaction is observed, one would assume the first step to be restate [19].

Tertiary amines in reaction of  $CO_2$  form unstable carbamate. The  $CO_2$  absorption rates of tertiary amines can be reached with activators. Low rates of  $CO_2$  absorption make tertiary amines difficult to use for  $CO_2$  gas removal. If the absorption rates for the tertiary amines could be increased efficiently while maintaining small heats of reaction, the absorbent regeneration energy could be greatly reduced [18, 19].

### *1.2.3 Role of amino acid ionic liquids (AAILs)*

Amino acid ionic liquids (AAILs) are particular representatives of amine-functionalized ILs. Amino acid exhibited potential benefits over amines owing to their lower vapor pressure. They are more tolerant to oxidative degradation and less toxic than traditional solvents [18, 20]. Ionic liquids comprised of ammonium cations or anions of naturally occurring amino acids containing an additional amine group such you see in Figure 1.2, (for example lysine, glycine, histidine or glutamine) were examined as high-capacity absorbents for  $CO_2$ . The absorption capacity increased and this demonstrated that desorption is possible under  $CO_2$ -rich conditions. The studies have revealed that the carbamic acid was formed with  $CO_2$  in ILs by chemisorption. It is emphasised that amino acid-carboxyl groups on the anion plays an important and different role in the catalyst for the sorption [21]. The crucial point in the amino acid molecules is the chiral centre that allows a great design of the molecules.

Herein, there are many works that seek to explain the effect of amino acid in ILs for the  $CO_2$ . Saravanamunughan et al.[21] show the synthesis of new amine-functionalized amino acid-based ILs and their super equimolar  $CO_2$  absorption capacity of 2 mol  $CO_2$  per mol IL at room pressure. They have used naturally the amino acid like lysine (Lys), histidine (His), asparagine (Asn), glutamine (Gln) for  $CO_2$  absorption. Those amino acids are considered monofunctional, because they contain only one amine group in addition to the amino acid functionality. The arginine (Arg) contains several additional amine groups; the methionine (Met) has not any additional amine group and it is considered not functional. They have used the lysine-based IL triethyl(tetradecyl)ammonium lysinate. The  $CO_2$  sorption experiments are performed with 1-2 g of neat amino acid-based ILs in a closed vessel by bubbling  $CO_2$  through the liquid at various temperatures. The carbon dioxide absorption capacity was calculated with a balance by the measure of the vessel's during the experiments [21].

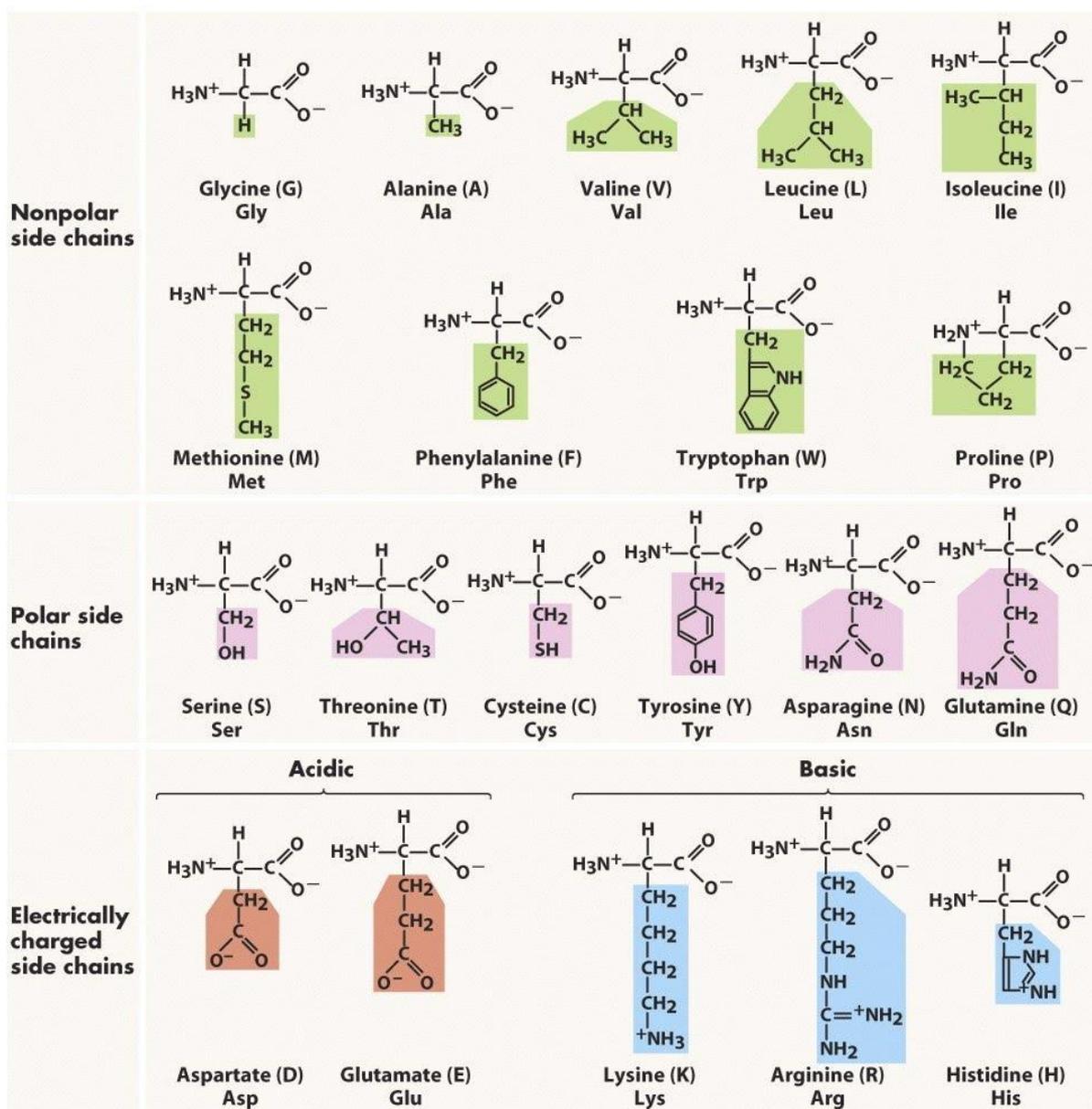


Figure 3-5 Biological Science, 2/e

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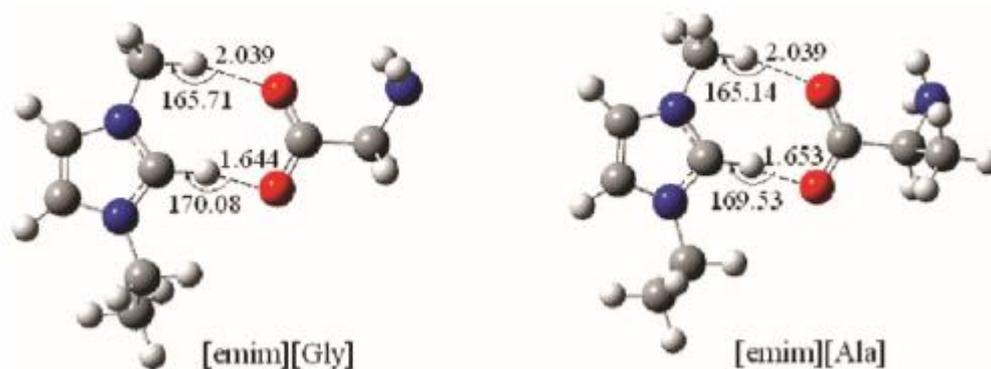
Figure 1.2: Classification of Amino Acid. Reported from Ref[22]

Bates and co-workers were the firsts that have functionalized an amine ILs. They reported an amine functionalized IL with a primary amine on the imidazolium cation captured CO<sub>2</sub> and they showed that capture was better. They obtained 0,5 moles of CO<sub>2</sub> per moles of IL. This result was similar to the case of standard amine scrubbing agents in which one CO<sub>2</sub> reacts with two amines. [23]

Zhang et al. used several tetrabutylphosphonium-based amino-acid ILs to absorb CO<sub>2</sub>. Phosphonium is a type of cation used for RTILs, this ion is stable in a basic environment at high temperatures than ionic liquids with amino acid than cations containing nitrogen, such imidazolium. In their work, a series of phosphonium ionic liquids with amino acid as anion were synthesized. They investigated the interaction between the ionic liquids and silica gel. The reaction between carbon dioxide and the system was examined. The rates of carbon dioxide

absorption of the supported ionic liquids were much higher than those of the viscous ionic liquids themselves. [24]

Wu *et al.* have studied the ionic liquids that have as anion 20 different amino acids. The ionic liquids containing 1-ethyl-3-methylimidazolium (EMIM) as cation and amino acid as anion. The optimized structures, energies, analysed in terms of their possible correlation with the interaction energies and the H-bond separation. The ion pairs of [EMIM][AA] can form strong H-bond interaction. Such interactions are dominated by the side-chain structure and the functional group of amino acid anions. The increase of the alkyl side-chain length corresponding with a decrease of H-bond energy. The functional groups lead to different localized charges on the anions. The intermolecular H-bond in amino acids can weaken the interaction, owing to the carbonyl O atoms a decrease in their proton-accepting ability. In the Figure 1.3 it is shown the interaction between atoms, their properties bonds (length and angle). The H-bond chemical nature of [EMIM][AA] was investigated by atoms in molecules and natural bond orbital analyses. It was shown that the absorption trend follows the cation type as DMIM > EMIM > PMIM [25].



**Figure 1.3:** Illustration of [EMIM][AA] with Glycine and Alanine, are shown the bond length in Angstrom and the bond angle. Adapted from Ref. [25]

Gurkan *et al.* in their work, investigated other type of ILs for carbon dioxide capture. They examined the aprotic heterocycle containing in the anion and compared the propriety of different molecules that have this structure. Aprotic heterocycle anions (AHAs), offer a highly versatile and tunable platform for the development of CO<sub>2</sub> capture. A series of AHAs paired with a phosphonium-based cation were investigated as potential absorbent for CO<sub>2</sub> capture from post combustion flue gas. A significant part of the cost operating is the energy required in the regeneration step so the ability to control the binding energy between AHA ILs and carbon dioxide has been investigated. The binding energy is influenced by the viscosity of AHA ILs. They have synthesized ILs bearing an alkyl-phosphonium cation with indazolide, imidazolide, pyrrolide, pyrazolide and triazolide-based anions that span a wide range of predicted reaction enthalpies with CO<sub>2</sub>. Each AHA-based IL was characterized by NMR spectroscopy and their physical properties (viscosity, glass transition, and thermal decomposition temperature) determined. In addition, the influence of substituent groups on the reaction enthalpy was investigated by measuring the CO<sub>2</sub> solubility in each IL. The AHA ILs show no substantial increase in viscosity when fully saturated with CO<sub>2</sub> at 1 bar. Taking advantage of the tunable binding energy and absence of viscosity increase after the reaction with CO<sub>2</sub>, AHA ILs are

promising candidates for efficient and environmental-friendly absorbents in postcombustion CO<sub>2</sub> capture. [26]

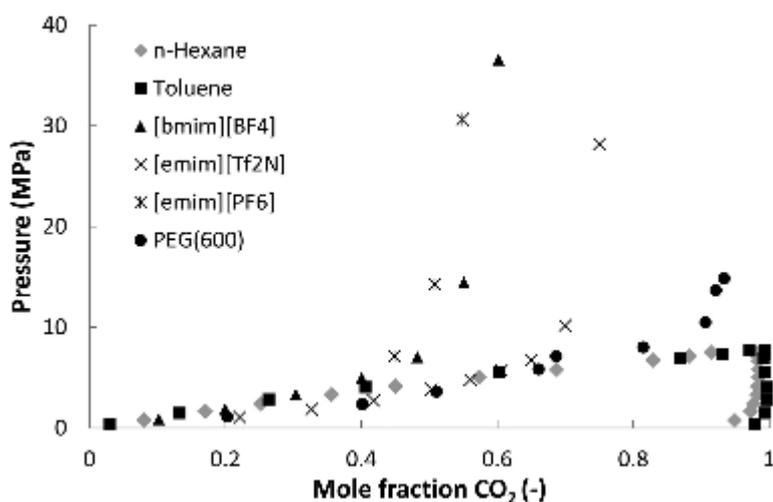
There is a recent work about cholinium-based amino acid liquids. Yuan et al. studied three cholinium-based amino acid ionic liquids: cholinium glycinate ([Cho][Gly]), cholinium alaninate ([Cho][Ala]) and cholinium proline ([Cho][Pro]). Each ILs was synthesized and characterized. The viscosity influenced the absorption. In this work the authors have explored the carbon dioxide absorption mechanism of aqueous solution [Cho][Gly] by Nuclear Magnetic Resonance. The results demonstrated that the both absorption and viscosity increased by increasing the IL concentration, while the apparent absorption rate constant decreases. The absorption loading decreased with increasing temperature. The absorption started with the chemical reaction to form the carbamate and followed by the hydrolysis of carbamate and CO<sub>2</sub> absorption. Each mechanism was compared to commercial absorbent with promising result. [27]

The cholinium- based amino acid ionic liquids have been studied for carbon dioxide capture, but in literature there are not information of the use of this novel solvent for the CO<sub>2</sub> reduction to CO. In this thesis work, we have first evaluated the absorption behavior of CO<sub>2</sub> in home-made prepared cholinium-based amino acid and, subsequently, we have investigated its use as electrolyte to potentially increase the CO<sub>2</sub> availability for the electrochemical reduction of CO<sub>2</sub>.

#### *1.2.4 Influence of physical factors*

The physical factors, as pressure and temperature have a high influence for CO<sub>2</sub> solubility and its utilization. In particular, the solutions of ILs have been evaluated and explored at different pressure, to figure out which is the better pressure range. In Figure 1.4 there is a graph that shows the behaviour of the capture of carbon dioxide vary with pressure, in different solutions.

The main finding was that the CO<sub>2</sub> solubility in conventional ILs based on a physical mechanism is still too low at post-combustion capture conditions to compete with the amine process. Furthermore, the Henry's constant tends to decrease with an increasing IL molecular weight, molar volume, and free volume [28]. Therefore, the CO<sub>2</sub> solubility in ILs should be compared on a molality (mol/kg) or molarity (mol/ m<sup>3</sup>) basis, instead of mole fraction basis. CO<sub>2</sub> absorption capacity has successfully been improved by functionalizing conventional ILs with an amine moiety, thereby allowing the CO<sub>2</sub> to react chemically with the amine.



**Figure 1.4:** Carbon dioxide capture in ILs vary with pressure. Reproduced from Ref [28]

To use for ILs for CO<sub>2</sub> separation, the carbon dioxide absorption capacity depends on pressure, temperature and molar ratio of solutions. The capture increases with increasing pressure and decreasing temperature. [1] This is evident when low-pressure CO<sub>2</sub> (1-2 bars) is put in contact with the IL, resulting in low CO<sub>2</sub> concentrations in the liquid phase.[11] As the increment of pressure increases, typically to up to 100 bar, the concentration of absorbed CO<sub>2</sub> increases. This displaying the general characteristics of a physical absorber [11, 17].

We must differentiate between the experiments at high and low pressure [29, 30]. For example, the solubility of carbon dioxide in the ionic liquid [BMIM][PF<sub>6</sub>] are presented for temperatures from (293 to 393) K and pressures up to about 9.7 MPa, showing purely physical solubility. Solubility pressures were correlated with an average relative uncertainty of about 1% by means of the extended Henry's law [31]. Every effort shall to avoid the use of high pressure, for the costs, the safety, the need of particular equipment.

The temperature influenced the viscosity. The ionic liquids have a very high intrinsic viscosity. The studies of ILs try to find a solvent with a low viscosity than common ionic liquids. There are many studies that utilizing room temperature, with ILs that have not need to further lower the viscosity [4, 32]. The viscosity of ionic liquids depends also of the structure of molecules (cations and anions) as well as the temperature and follows an Arrhenius's law [33]. The interactions between cation and anion can be electrostatic, hydrogen bonding or/and van der Waals bonding and this behaviour is only weakly influenced of the temperature [33].

The research of ILs is capable of carbon dioxide capture is focusing on low pressures. Our tests were performed with the solvents at atmospheric pressure and room temperature.

### 1.3 CO<sub>2</sub> electroreduction to CO

To increase the efficiency of the CO<sub>2</sub> electrochemical reduction, more studies are required to find electrolytes that increase the CO<sub>2</sub> solubility and reactivity in the catalyst surface. This should be coupled to electrochemistry studies, development of new catalytic materials and appropriate setup.

The performance of electrocatalysis is influenced by many parameters.

- Current density ( $j$ ): the quantity of electric charge per unit of time and area. A good catalyst should show a high current density at the reaction's potential;

$$j = \frac{\text{current}}{\text{area}} \quad (1.1)$$

- Overpotential ( $\eta$ ): it is defined as the difference between the thermodynamic reduction potential and the potential used during the experiment. The goal is to minimize the overpotential, therefore that the potential used during the experiment is more similar at the reduction potential of theory.
- Faradic efficiency (FE): it is the percentage that shows the selectivity of materials of the electrocatalyst. This is the ratio between the quantity of electric charge per unit time involved in the product's formation and the total electric charge per unit time. If the FE is high we can say that in the system don't exist parasitic reactions.

$$FE = \frac{\text{production rate} \cdot Z \cdot F}{j \cdot \text{time}} \quad (1.2)$$

Where the production rate is the moles/mass of the considered species, produced per unit time and unit surface area of the electrode;

$Z$  is the number of electrons involved;

$F$  is the Faraday constant.

Carbon dioxide can be electrochemically reduced to a variety of products as carbon monoxide, methanol, acetic acid. However, the carbon dioxide molecule is very stable, linear and centrosymmetric. The carbon-oxygen bond is shorter than a single bond and it is shorter than most C-O multiply bonded functional groups. Since it is centrosymmetric, the molecule has not electrical dipole. Since the molecule is very stable, carbon dioxide requires a high energy quantity to spend in the electroreduction. The reduction of  $\text{CO}_2$  to  $\text{CO}$  is ordinarily a difficult and slow reaction.

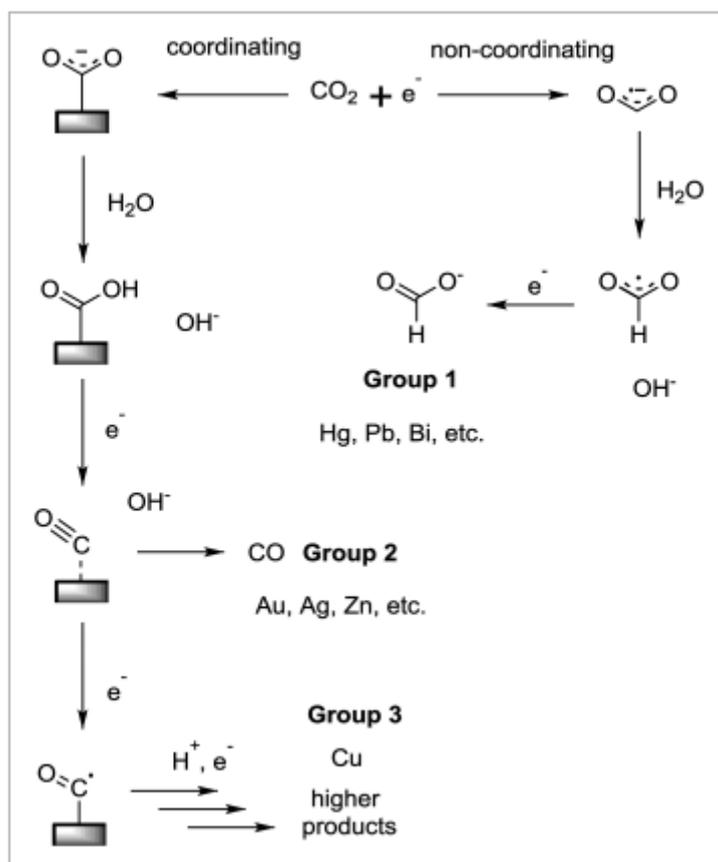
Generally, an electrochemical  $\text{CO}_2$  conversion system is composed of a cathode part where  $\text{CO}_2$  molecule is directly reduced to other chemicals on the catalyst surface. The catalyst surface may be of noble expensive materials as Ag, Au, Cu, Zn. The anode part where counter oxidation reaction takes places: here occurs the water oxidation in aqueous system. These two cathode and anode part are present both in the same reaction medium or separated by a proton exchange membrane to take an advantage of independent variation and optimization for each part. The development of high performance electrochemical  $\text{CO}_2$  reduction is investigated, but these systems have not commercial level regarding efficiency. The most critical bottleneck is the high thermodynamic stability of carbon dioxide molecule. This bottleneck means that electron injection into  $\text{CO}_2$ , which is the first reduction step of  $\text{CO}_2$  electrochemical conversion, is significantly disfavoured. [4]

To solve this problem, investigations on novel catalyst materials coupled to improved electrolytes are on-going in the scientific community.

### 1.3.1 CO<sub>2</sub> mechanism on metal electrodes

The kinetic barriers for the CO<sub>2</sub> activation can be relaxed by finding catalysts that can break the linear symmetry of CO<sub>2</sub> molecule and favour the C-H bond formation. For the primary reduction of CO<sub>2</sub>, it is required a change in a molecule geometry, from linear to the bent radical of CO<sub>2</sub><sup>-</sup>. This structural change needs of significant overpotential. It is obtained that there are three groups of catalysts, and each group favoured one specific product. The formation of the CO<sub>2</sub><sup>-</sup> intermediate is considered very important, it is the first limiting step, and its coordination determines whether the 2e<sup>-</sup> reduction will proceed towards the production of CO.[29]

Jones et al. divided the possible catalysts in three groups. In Figure 1.5 we can find the different characteristics of metals and their behaviour with carbon dioxide. The first group is constituted of metals such as Pb, Hg, In, Sn, Cd, that they cannot bind to the intermediate. These metals produced formic acid as main product. The metals as Au, Ag, Zn and Ga are included in the second group and they're able to bind to CO<sub>2</sub><sup>-</sup> intermediate but they cannot reduce CO. In the third group there is only one metal, Cu, that can bind with intermediate and reduce CO to products, such alcohols. Other metals are excluded from the carbon dioxide reduction because with aqueous electrolyte they are active to water splitting [2, 29]. In this contest the different choice of catalyst influenced the carbon dioxide reduction and the ratio between H<sub>2</sub>/CO.



**Figure 1.5:** Classification of metal catalysts based on their mechanism for electrochemical CO<sub>2</sub> reduction. Reproduced with permission of Ref. [29] Copyright (2014), John Wiley and Sons.

In particular, it is investigated Au and Ag for CO production, since they are not able to further reduce CO to other products. Such materials are expensive and low-abundant. To solve this problem, it is possible to deposit noble materials in the form of nanoparticles. The use of nanoparticles minimized the quantity that is required of the expensive materials. Also reduce the costs, the use of optimized structure influenced the performance, increased conductivity, improve the mass transport and reduced the overpotential [34].

In recent works, it is bind the important influence of catalyst and co-catalyst. Co-catalyst can be a supported such Titania or electrolyte. [1, 2, 32, 35]

### *1.3.2 The role of ILs as electrolyte*

The electrolyte isn't solely the medium between anode and cathode parts, it has an important role in CO<sub>2</sub> reduction. [4, 36]

Electrochemical carbon dioxide reduction into chemicals has been actively investigated due to its potential for converting waste CO<sub>2</sub> captured from emissions into other products.

Due to extreme stability of the molecule, it is required high potential (-1,9V vs SHE) to apply CO<sub>2</sub> reduction, because the first electron reduction involves the bending of the linear CO<sub>2</sub> molecule to form the radical anion. Common aqueous electrolytes, which are generally composed of alkali cations (e.g. Na<sup>+</sup>, K<sup>+</sup>), various anions, such as halide anions, bicarbonate (HCO<sub>3</sub><sup>-</sup>) or hydroxide (OH<sup>-</sup>), are employed for the heterogeneous electrochemical reduction of CO<sub>2</sub>, due to their high conductivity in water. Water itself can be a source of proton exchange. Hence, the employed electrolyte plays a key role in the production and selectivity of different products. The choice of the electrolyte can have a profound effect on the current density and selectivity of the CO<sub>2</sub> reduction products. [2]

Zhao et al. used for the first time the room temperature ionic liquids as electrolytes for the electrochemical reduction of high pressure carbon dioxide. They obtained high solubility of carbon dioxide and good intrinsic ionic conductivities. Zhao et al. demonstrate that CO<sub>2</sub> and water can be converted into CO and H<sub>2</sub> electrochemically using 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM PF<sub>6</sub>) as an electrolyte. After the electrolysis, the products can be easily recovered without cross-contamination, leaving BMIM PF<sub>6</sub> in the electrolysis cell, and the IL can be reused without further treatment. This method provides a new and clean route to convert H<sub>2</sub>O and CO<sub>2</sub> into valuable chemicals [37]

Following the pioneer work of Zhao many researches add ILs in the medium used as electrolyte. Rosen et al. investigated carbon dioxide reduction to CO, they used a silver as working electrode and 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM BF<sub>4</sub>) with water as electrolyte. The experiment shall be carried out at atmospheric pressure. This work shows that the ionic liquid lowers the energy of the CO<sub>2</sub><sup>-</sup> intermediate thereby decreasing the initial barrier to reduction. This study demonstrates that the water was a proton source at overpotentials as low 0,2V with Faraday efficiency higher than 96 %. [36, 38]

Medina-Ramos showed that the ability of the ionic liquid used in their tests was to contribute in the conversion of carbon dioxide in CO. Their work demonstrates that 1,3-dialkylimidazoliums can promote CO production, but only when used in combination with an appropriately chosen electrocatalyst material. More broadly, these results suggest that the

interactions between CO<sub>2</sub>, the imidazolium promoter, and the cathode surface are all critical to the observed catalysis [39].

Medina-Ramos in their previous work [40] were focused into inexpensive materials used as cathode such as Bismuth. Gold and silver have historically been the most active cathode for CO<sub>2</sub> reduction, but bismuth presents itself as an affordable and environmentally benign metal. In other words, showed that electrochemically prepared Bi and Sn catalyst were highly active and selective in presence of BIMIM triflate (OTf) in acetonitrile solution for CO production [36, 39].

Watkins et al. demonstrated that the ionic liquid, 1-ethyl-3-methylimidazolium trifluoroacetate can act as an effective medium for the carbon dioxide reduction to formate. The ILs was used with water presented as a “cosolvent”. The electrolysis mixture consisted in 33% of water and it influence the formate concentration. The mechanism for this high yielding reduction of CO<sub>2</sub> was proved not to involve a C-2 bound carboxylate intermediate. The behaviour was attributed to a stabilizing effect of the ionic liquid on the carbon dioxide intermediate and the increased solubility of carbon dioxide in the matrix. They examined indium, tin and lead: metals and found that they have similar properties for formate production. Tin showed very similar behaviour to that seen for indium and lead showed an increased Faradaic efficiency for formate but at more negative applied potential [41].

Barrosse-Antle *et. al.* studied the electrochemical CO<sub>2</sub> reduction in 1-butyl-3-methylimidazolium acetate and they demonstrate that the mechanism of reaction was not sustainable. They observe that gaseous CO<sub>2</sub> is irreversibly absorbed by BMIM Acetate, but this ILs suggests a means for the sequestration of the greenhouse gas [42].

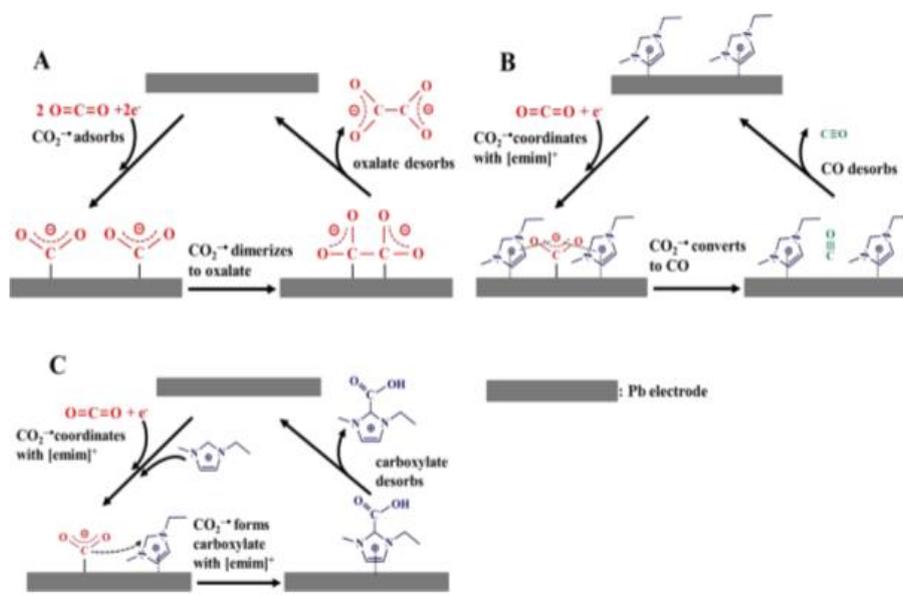
Hollingsworth et al. used a reactive ionic liquid as the solvent for the electrochemical reduction of CO<sub>2</sub> with silver electrode. They utilized the superbasic tetraalkyl phosphonium ionic liquid and they observed that it can chemisorb carbon dioxide through the characteristic binding with the 1,2,4-triazole anion. The silver electrode is reduced by CO<sub>2</sub> chemisorbed and it was form formate at low overpotential [7].

The literature shows that the major products of carbon dioxide reduction in ionic liquids based electrolyte are formate and carbon monoxide. Pardal et al. show that the bimetallic cathode (Zn-Cu) have an electrochemical activity for CO<sub>2</sub> reduction in a bath of BIMIM triflate [36].

Sung et al. in their recent work observe that the great effects for catalysis are owing at an incorporation of intramolecular imidazolium groups into carbon dioxide reduction. They hypothesize that the incorporation of charged, slightly acidic, and redox-active imidazolium groups into the secondary coordination sphere of molecular complexes may provide alternative path to tune redox potentials as well as allow for synergistic intramolecular interactions between reactive metal sites, imidazolium, and CO<sub>2</sub> substrate molecules [43].

Sun et al. observe that the presence of ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][Tf<sub>2</sub>N].) used with lead cathode shows the catalytic role of ionic liquid in shifting the course of the reduction pathway. The cyclic voltammograms confirm that imidazolium IL lowers the overpotential for CO<sub>2</sub> reduction by about 0.18 V. In the Figure 1.6 is showed that the mechanism of the possible electrochemical reduction of CO<sub>2</sub> can be altered dramatically by the presence of [EMIM][Tf<sub>2</sub>N]. Specifically, increasing the concentration of IL in 0.1 M changed the products, in fact [EMIM][Tf<sub>2</sub>N] switches the product

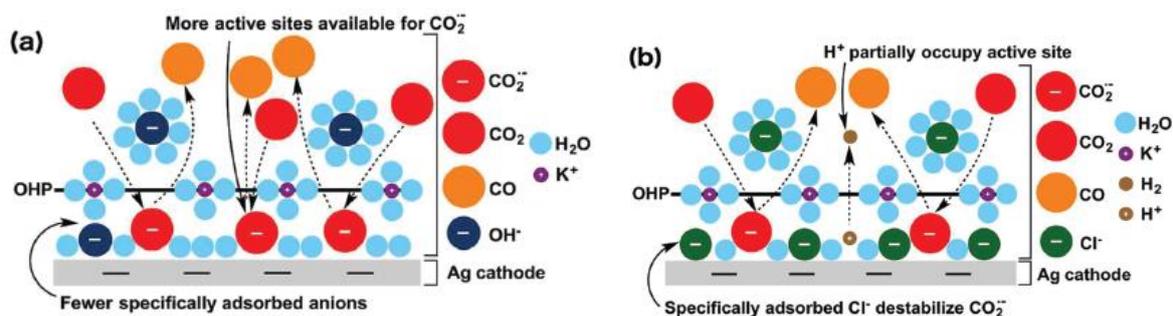
from oxalate to CO and an imidazolium carboxylate complex. The oxalate was considered the main product of CO<sub>2</sub> reduction on lead catalyst in acetonitrile without ionic liquid as solvent [44].



**Figure 1.6:** Different pathways of electrochemical CO<sub>2</sub> reduction. Comparison between common solvent and [EMIM][Tf2N] as electrolyte on Pb electrode. Reproduced from Ref.[44].

The work of Verma *et. al.* reported the effect of electrolyte composition on the electroreduction of carbon dioxide to carbon monoxide on silver based gas diffusion electrodes [3]. They observe that increasing the IL's concentration in the electrolyte leads to an increase in current density irrespective of the nature of the anion. They use electrolyte as KOH, KHCO<sub>3</sub> and KCl and anions play a key role in the process with the onset potential for CO formation. The activity trend with respect to the different cations was  $\text{OH}^- < \text{HCO}_3^- < \text{Cl}^-$ . [3]

In Figure 1.7 we can see the behaviour of different ions ( $\text{Cl}^-$  and  $\text{OH}^-$ ). The small anions such  $\text{OH}^-$  tend to interact with the silver surface with electrostatic forces and are housed beyond the Outer Helmholtz Plane (OHP), instead solvated anions such ( $\text{Cl}^-$ ) tend to interact with a specific absorption with electrode surface. The absorption of  $\text{Cl}^-$  on silver surface is more favourite than  $\text{OH}^-$  for the Gibbs free energy [3].



**Figure 1.7:** Schematic process of  $\text{KOH}$  (a) and  $\text{KCl}$  (b) as electrolyte in  $\text{CO}_2$  reduction with silver electrode. Reproduced from Ref. [3] with permission of Royal Society of Chemistry.

In this thesis work we focused on the choice of electrolyte and the decision is influenced by the possible interactions between the cathode electrode and the considered ionic liquid.

This thesis is focused on carbon dioxide absorption and its utilisation through the electrochemical reduction process into CO. To reach our goals, a novel ionic liquid, i.e. Choline Glycine, has been used. The conventional solvents used in industries are amine solutions. Instead, ionic liquids are a new generation of solvents that show promising properties in  $\text{CO}_2$  absorption and in electrocatalysis. In this work, the ChoGly solution was used in an absorption process for capturing  $\text{CO}_2$  and as an electrolyte in an electrochemical cell for reduction of  $\text{CO}_2$  into CO.

It has been studied the absorption capacity of ChoGly solution with different concentrations of it in water, at different operating temperatures and with different electrolytes.

The second objective of this thesis is to evaluate the feasibility of the electrochemical reduction of  $\text{CO}_2$  to CO by using the ChoGly solution as an electrolyte. It was assumed that a solution with highest absorption capacity for  $\text{CO}_2$  could have the higher CO production rate as well.



## 2. Synthesis of AAILs

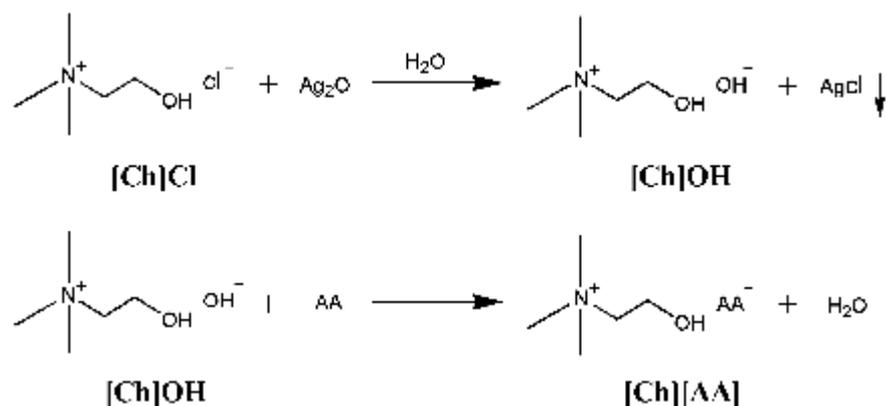
We were focusing on ionic liquids that contain the amino acid, because they are more environmentally friendly than common ILs. The ILs AA are less toxic and less damaging to the environment and health.

The first synthesis of ionic liquid obtained from 20 amino acid was reported by Fukumoto et al. [45]. They obtained the amino acid ionic liquid and they found that the AA ILs were miscible in many organic solvents. They used as cation [EMIM], but this miscibility of this newly structure is due to the presence of imidazolium and/or carboxylic groups. This allow amino acids to be used in many applications. The choice of the cation is important and there are many works that use choline in their molecule's structure.

De Santis and al. [8] used two methods for the synthesis. The first method was found in the literature: the aqueous solution of choline hydroxide, with concentration 4M, was added dropwise with cooling to an amino acid aqueous solution or suspension to obtain a slightly excess (10% mol) of amino acid. The mixture was stirred. Water was then removed under reduced pressure at 50 °C with a rotavapor. Acetonitrile/methanol was then added with vigorous stirring to precipitate the excess of amino acid. The mixture was left stirring overnight and the excess of amino acid was then filtered off. Filtrate was evaporated to remove solvents at 50 °C. The product was dried in vacuo for 24 h at 50 °C. The second method is based on a potentiometric titration. An aqueous solution of choline hydroxide (2,5 M) was titrated by adding AA. Between each AA aliquot we waited to obtain complete solubilization of AA (usually less than 1 min). In the proximity of the equivalence point each AA addition was reduced to about 1 mol% of the stoichiometric amount required for titration.

Tao et al. [46] in their work prepared five AAILs that contain choline as cation, and respectively glycine, two different enantiomers of alanine, proline and serine as anion. The Figure 3.1 shows the procedure of synthesis. This synthesis consists in two steps.

*First step:* an aqueous solution of [Cho]OH was obtained from metathesis of [Cho]Cl (0,05 mol) with Ag<sub>2</sub>O (0,025 mol);

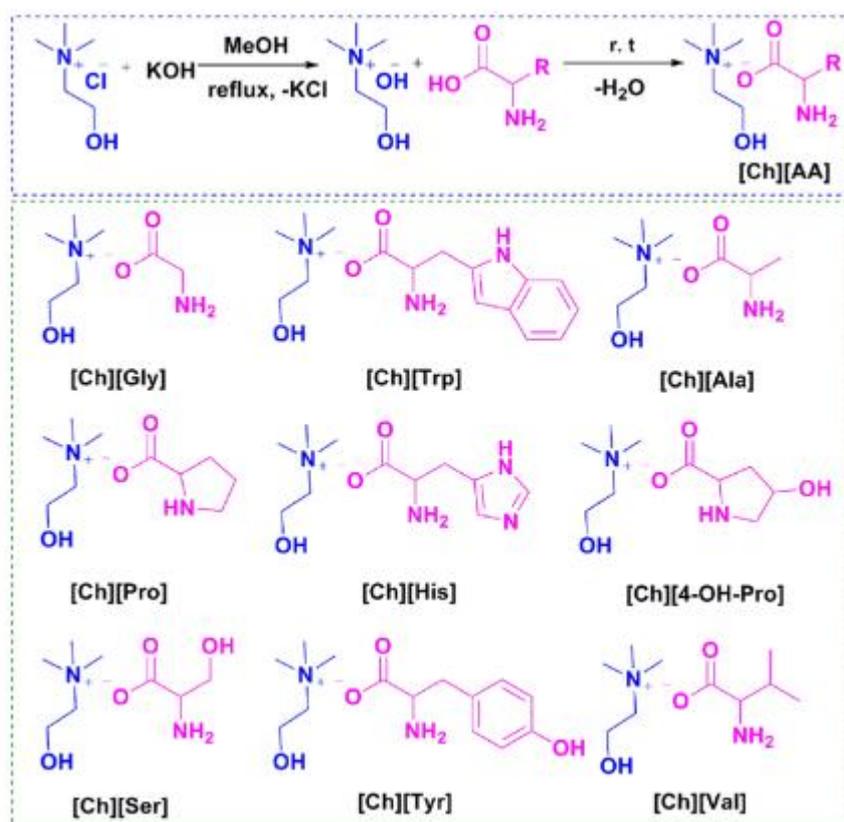


**Figure 2.1:** Procedure of synthesis of [Ch][AA]. From Ref.[46]

*Second step:* the solution was centrifugated and filtered. The [Cho]OH containing filtrate was then neutralized with solution of amino acid by stirring for 12h at room temperature. The water

of solution evaporated under vacuum and the excess of amino acid was precipitated by adding ethanol. AAILs contain the residuals that are removed.

Saptal et al. [47] in their work describe the method of synthesis that they have used (Figure 3.2). In a solution of Cho Cl (1 equivalent) was added the methanol potassium hydroxide (1.2 equivalents), at room temperature with constant stirring. The temperature of the reaction increased gradually up during the experiment. After 12h, time of experiment, the reaction mixture cooled room temperature and KCl was filtered. The choline hydroxide in methanol solution was added drop wise into the amino acid solution at 5°C. The reaction mixture was then kept for other 40 h in order to have the neutralization reaction with stirring. The water was removed under the reduced pressure and Saptal obtained ILs. The AAILs was cleaned with ethyl acetate as solvent.



**Figure 2.2:** Procedure of synthesis of [Ch][AA]. From Ref [47]

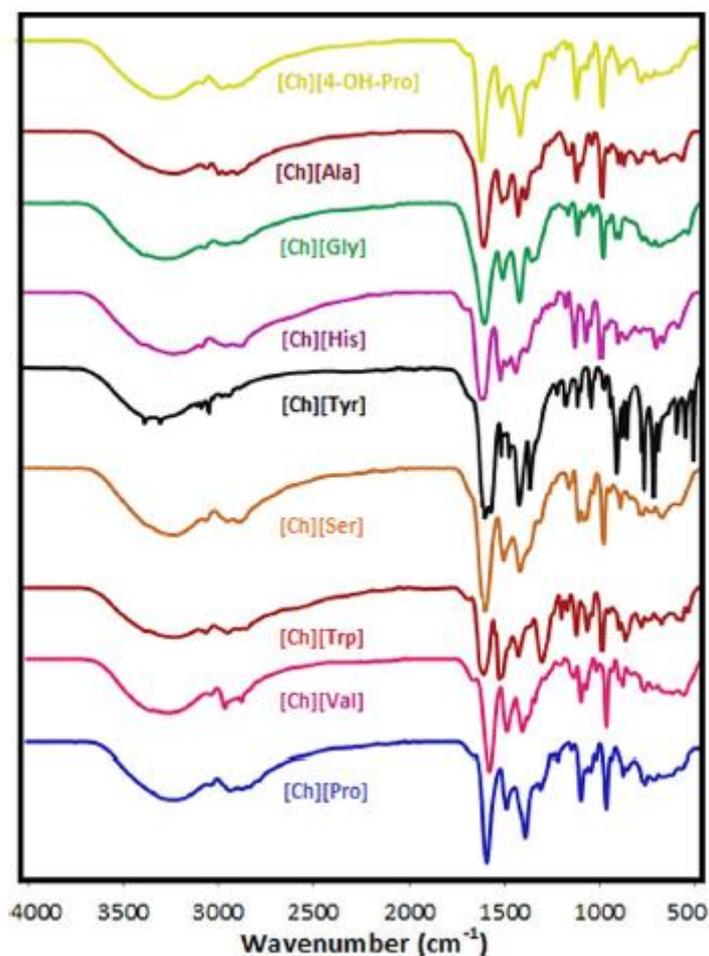
In this thesis work it was used the ionic liquid synthesized in IIT's laboratory (Istituto Italiano di Tecnologia). The ionic liquids have been prepared by Sergio Bocchini with a novel method that is similar to the procedure describes by Saptal, but the new synthesis' technique presents some difference.

Glycine and potassium hydroxide (1.2 equivalents) were added at room temperature to ethanol with constant stirring. Then, after 6 h the choline chloride solution (1 equivalent, analytical grade). After 4 h KCl was separated by centrifugation. The ethanol and water were removed by evaporation and then kept under the reduced pressure (0,5 bar).

## 2.1 Characterization of AAILs

To make certain that the solution synthesized is effectively an ionic liquid solution, the characterization is necessary.

In the paper of Tao [46] the characterization of AAIL solution confirmed the presence of ILs by H NMR, elemental analysis, and FT-IR spectra. The ILs synthesized with a method of Saptal et al. [47] were characterized by using various analytical techniques including nuclear magnetic resonance (NMR), spectroscopy and FTIR that was illustrate in Figure 2.3. The figure shows the difference between various functional groups of the molecule that present a respectively wavenumber.



**Figure 2.3:** Comparison of IR data of the synthesized AAILs. From Ref.[47]

Thanks to a characterization we can be sure of the presence of specific AAILs.



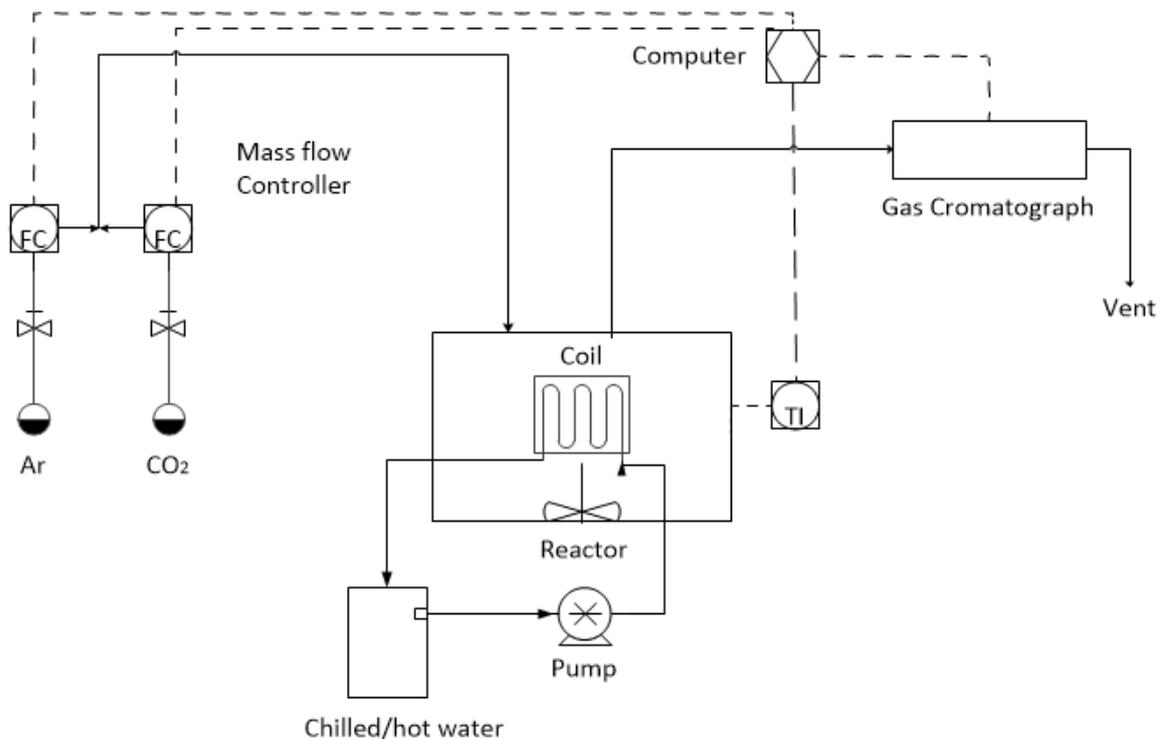
### 3. Absorption of CO<sub>2</sub> experiment

The first step in converting the carbon dioxide into CO is the absorption of the CO<sub>2</sub> in a solvent. The literature indicates different solutions that have the potential to absorb the carbon dioxide. The ionic liquid solutions are the promising solvents to this goal. The task specific ILs have been studied to understand how they allow the formation of chemical bonds in order to improve the overall absorption capacity during the capture process [48]. In this thesis we perform experiments at the laboratory of “Solar Fuel Lab” in Polito in order to see the CO<sub>2</sub> Capture capacity of the specific Ionic studied in this work..

#### 3.1 Absorption setup

The experiments have been performed with a particular setup. This setup consists of:

- Reactor;
- Heating Coil element
- Pump connected to the reactor’s coil;
- Gas Chromatograph (GC);
- Mass flow controller (2 MFC);



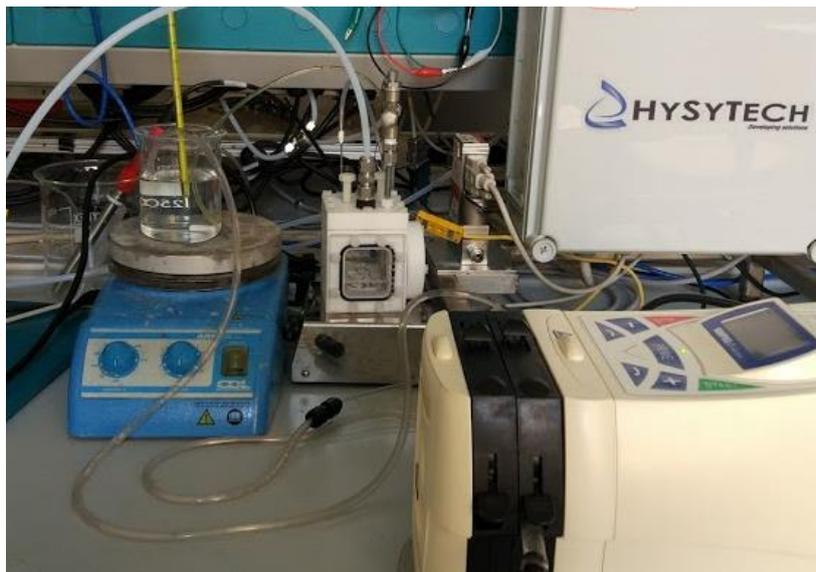
**Figure 3.1:** *Conceptual scheme of the setup of CO<sub>2</sub> Absorption*

The reactor is filled with 40 ml of solution. The temperature inside the reactor is kept constant during the test by using a coil (Figs 3.1-3.2). The peristaltic pump (Gilson MINIPULS® evolution) pumps the water to the coil. The pump use for every test the same amount of velocity (10 RPM). The absorption of CO<sub>2</sub> is an exothermic reaction though the temperature is tending to increase.

Before the experiment, Argon flux (50 ml/min) was sent in to the reactor to outgas it from the air. Before starting the experiments, the concentration of nitrogen in the system where verified and it was ensured a minimum level of about 800 ppm.

A mixture of CO<sub>2</sub> and Ar were sent into the system consisting of 25% CO<sub>2</sub> and 75% Ar in a 40 ml solution. The mass flow controller (Bronkhorst EL-FLOW model F-201CV) is calibrated for N<sub>2</sub> gas, it has used the conversion factors that the producer provides.

The reactor was connected to Gas Chromatograph. The GC reads the CO<sub>2</sub> concentration that is present in the top of the reactor. The CO<sub>2</sub> concentration grows up with time and when the value of the CO<sub>2</sub> out is equal to the value of the CO<sub>2</sub> in, the solution is saturated (or achieved equilibrium).



**Figure 3.2:** Setup of CO<sub>2</sub> Absorption.

### *3.2 Blank: solution of H<sub>2</sub>O*

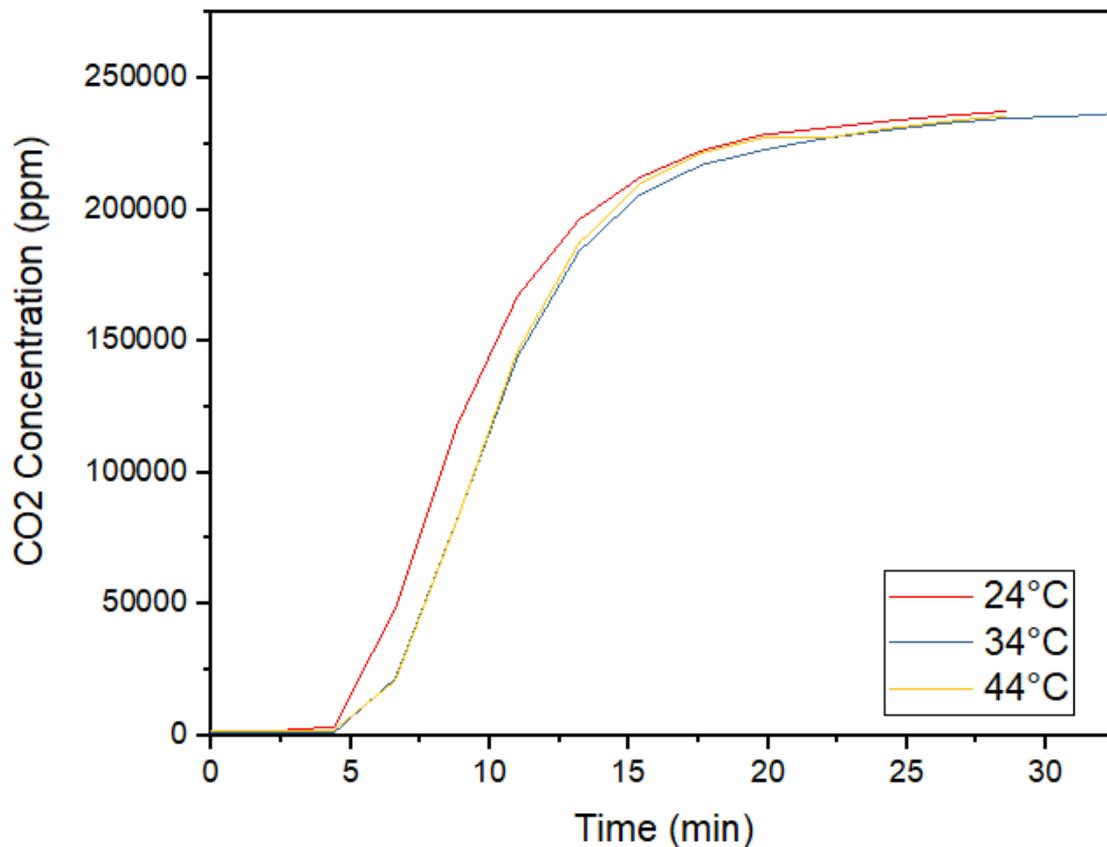
It was prepared a blank solution with water and absorption experiments were carried out on H<sub>2</sub>O blank solution at different temperatures: 24 °C, 34 °C, 44 °C. The tests with blank solution are performed to understand the response time of the system (time lagged between the input and output reading of the system).

The reactor is filled with 40 ml of H<sub>2</sub>O bidistilled by Direct-Q System Millipore and the test starts once the CO<sub>2</sub> valve is open. The GC initially reads a concentration of CO<sub>2</sub> near zero, after 4.4 minutes minutes the CO<sub>2</sub> Concentration curve grows rapidly because the CO<sub>2</sub> absorption capacity of blank solution is low compared to the other solution studied for CO<sub>2</sub> absorption.

The Figure 3.3 shows that the break through is happening at 4.4 minutes. Furthermore from Figure 3.3 it can be noted that the break through point is the same for different temperatures. From the break through curve one can evaluate the amount of CO<sub>2</sub> absorbed by integrating the area under the break through curve (Figure 3.3) The weight of CO<sub>2</sub> absorbed with 40 ml of blank solution of water is reported in Table 3.1 for a flux of Ar and CO<sub>2</sub> with volumetric velocity of 10 ml/min. In this table it can also be noted that, in contrast with the theory, in those tests CO<sub>2</sub> absorption slightly increases along with temperature, which can only be justified by the intrinsic experimental error in these measurements (calculated to be of at least of 0.154 g).

**Table 3.1:** CO<sub>2</sub> absorbed in Blank Solution at different temperatures

T [°C]	CO <sub>2</sub> absorbed [g]
24	0,1449
34	0,1596
44	0,1633



**Figure 3.3:** Concentration of CO<sub>2</sub> outgoing from reactor vs time. Comparison between different temperature in a solution of H<sub>2</sub>O (Blank solution).

### 3.2.1 Data elaboration

The GC connected to its software reads the CO<sub>2</sub> concentration in ppm or %mol with respect to time. The period of time is equal to 2.2 minutes.

From the mass balance is possible to evaluate the quantity of carbon dioxide absorbed from the solution. We know the % of CO<sub>2</sub> that is sent in the reactor.

$$Q_{tot\ in} = Q_{Ar\ in} + Q_{CO2\ in} \quad (3.1)$$

$$Q_{tot\ in} = Q_{Ar\ in} + Q_{tot\ in} \cdot X_{CO2} \quad (3.2)$$

Where:

$Q_{tot\ in} \left(\frac{Nl}{s}\right)$  is the total flow rate sent to bubbling in the solution;

$Q_{Ar\ in} \left(\frac{Nl}{s}\right)$  and  $Q_{CO2\ in} \left(\frac{Nl}{s}\right)$  are the flow rate of Ar and CO<sub>2</sub> respectively;

$X_{CO2} (\%)$  is the percentage of CO<sub>2</sub> at the output.

The quantity of CO<sub>2 out</sub> is evaluated as follows (Equation 3.3)

$$Q_{CO2\ out} = \frac{Q_{Ar\ in} \cdot (X_{CO2\ out})}{1 - (X_{CO2\ out})} \quad (3.3)$$

Where:

$Q_{CO2\ out} \left(\frac{Nl}{s}\right)$  is the flow rate of CO<sub>2</sub> in the output;

$CO2_{out} (\%mol)$  is the CO<sub>2</sub> concentration reading from GC.

From mass balance follows the  $Q_{CO2\ abs} \left(\frac{Nl}{s}\right)$  (Equation 3.4) can be written as:

$$Q_{CO2\ abs} = Q_{CO2\ in} - Q_{CO2\ out} \quad (3.4)$$

The cumulative mass of absorbed CO<sub>2</sub> was determined with applying cumulative integral on the break through curve (concentration vs time) as shown in Figure 3.3. The mass of absorbed CO<sub>2</sub> in the solution of ChoGly is calculated and reported as the ration of moles of CO<sub>2</sub> absorbed per moles of IL.

The total mass of absorbed CO<sub>2</sub> is calculated as following (Equation 3.5);

$$m_{CO2\ abs} = \frac{V_{CO2\ cum} \cdot PM_{CO2}}{V_m} - m_{CO2\ abs\ Blank} \quad (3.5)$$

Where:

$m_{CO2\ abs} (g)$  ;

$V_{CO2\ cum} (Nl)$  ;

$PM_{CO2} (g/mol) = 44$ ;

$V_m (l/mol)$  for the ideal gas is equal to 22,4.

The  $m_{CO_2 \text{ abs Blank}} (g)$  is calculate by Equation 3.6.

$$m_{CO_2 \text{ abs Blank}} = \frac{V_{CO_2 \text{ cum}} \cdot PM_{CO_2}}{V_m} \quad (3.6)$$

In these calculations the response time of the system obtained from the CO<sub>2</sub> absorption tests in blank solution of water was considered.

Finally, the absorption capacity of the solution was calculated (Equation 3.7).

$$Absorption \ Capacity = \frac{n_{CO_2 \text{ reactor}}}{n_{IL \text{ solution}}} \quad (3.7)$$

Where Absorption Capacity of CO<sub>2</sub> is the ratio between the moles of CO<sub>2</sub> absorbed by the IL in the system and the moles of ionic liquid in solution.

It has been calculated the qualitative absorption of CO<sub>2</sub> by the Equation 3.8 by weighting the solution before and after the tests.

$$\%CO_2 \text{ absorbed} = \frac{W_{finish} - W_{initial}}{W_{initial}} \% \quad (3.8)$$

Where:

$W_{finish} (g)$  is the weight achieve a saturated solution;

$W_{initial} (g)$  is the weight of fresh solution.

### 3.3 Absorption performance of CO<sub>2</sub> in aqueous Choline Glycine solution

In this thesis our focus is on the Choline Glycine behaviour and its capacity to absorb the CO<sub>2</sub>. For this reason several tests were performed in different conditions by modifying the concentration of ionic liquid, the temperature of the system and the space velocity of the input flow. In addition the results from the experiments were compared to the results reported in the literature.

#### 3.3.1 Absorption performance in a different Concentration of Choline Glycine solution

A set of solutions (40ml) of water and Choline Glycine with different volumetric percentage have been prepared as shown in Table 3.2. The gas flow mixture has been introduced into the reactor with flow rate equal to 40 ml/min of which 25% is the CO<sub>2</sub> corresponding to approximately 255000 ppm at constant temperature of 24°C. The temperature of the reactor is kept constant with a coil during the test. It has been noted that the Choline Glycine has a persistent typical smell, high viscosity and density (1122 g/l).

Furthermore, the amount of absorbed gas was measured in two ways. In the first method the absorbed CO<sub>2</sub> is calculated from the integral of the break through curve. While in the second approach the absorbed CO<sub>2</sub> is evaluated by weighting the solution before and after saturation.

**Table 3.2: Solutions of Choline Glycine**

Concentration (v/v ChoGly/H <sub>2</sub> O)	Volume H <sub>2</sub> O [ml]	Volume [Cho][Gly] [ml]
10 %	36	4
20 %	32	8
30 %	28	12
40 %	24	16

### 3.3.2 Absorption performance at different temperatures

Has been investigated the behaviour of an aqueous solution of [Cho][Gly] with a concentration in volume equal to 20 % (v/v) at 24 °C, 34 °C and 44 °C. The temperature inside reactor is kept constant by using a coil and a pump. The peristaltic pump send the chill or hot water into the coil, in order to keep the temperature constant.

The Table 3.3 shows the density of CO<sub>2</sub> by varying temperature.

It should be noted that to qualitatively calculate the amount of CO<sub>2</sub>, 10 ml of solution was weighted at room temperature before and after saturation independently from the temperature of each test.

**Table 3.3: Density of CO<sub>2</sub> at different temperatures.**

Temperature [°C]	CO <sub>2</sub> Density [g/l]
24	1.7906
34	1.7312
44	1.6758

### 3.3.3 Absorption performance at different CO<sub>2</sub> flow rate

A set of experiments have been carried out using different flow rate of CO<sub>2</sub> equal to 5 and 10 ml/min for a solution of 10 and 20 vol/vol% concentration of CHoGly. The Table 3.4 shows the conditions of the experiment

**Table 3.4:** *Conditions of the CO<sub>2</sub> flow rates experiment*

CO <sub>2</sub> Flow Rate[ml/min]	%ChoGly Concentration v/v
5	10%
5	20%
10	10%
10	10%

### 3.3.4 Absorption of CO<sub>2</sub> performance of ChoGly with other solutions

Experiments were made by using different solutions based on ChoGly but containing typical electrolytes used for the electrochemical CO<sub>2</sub> reduction reaction. Water in solution has been replaced with different solvents, in order to define the one that better fits absorption needs. All solutions contained the same ChoGly concentration equal to 30% v/v. Table 3.5 lists all different solvents used in the experiment.

A series of tests have been done to investigate the CO<sub>2</sub> capturing behaviour of ChoGly in different solvents of KOH and KCl. The solvents chosen are a basic and a neutral electrolyte. The solutions were made with 30 % v/v of ChoGly and the rest of a KOH or KCl solution in water.

**Table 3.5:** *Different solvent used*

Solvent	Concentration [mol/l]
KOH	2
KCl	2



## 4. Electro-reduction experiment

In this section it's described how the electrocatalytic tests are developed. The chemistry laboratory where I have been able to work is the "Solar Fuel Lab". The setup consists in:

- Reactor;
- Potentiostat;
- Gas Chromatograph (GC);
- Mass flow controller;
- Reference.

The reactor is an electro catalytic cell where the reactions occur. The cell is a custom device realized in Teflon by Hysytech and it has a quartz window where the solar light, or a lamp, can light up the cathode in photocatalytic tests. The reactor is magnetically stirred and connected to a potentiostat (Biologic, VS.P-300) which applies the require potential. The potentiostat applies a potential difference between the working electrode (WE in Fig. 3.1) and the reference electrode (REF in Fig.3.1). The working electrode is the catalyst, a commercial silver foil (SIGMA-ALDRICH, silver foil, thickness 0,25 mm, 99.99%) and the reference is Radiometer Analytical, REF421 saturated calomel electrode), the counter electrode (CE in Fig.3.1) is a platinum spiral. The reactor is filled with solvent, the electrolyte and the gas, carbon dioxide, is bubbled into solution. As consequence of the inlet flow, a flow rate approximately equal to the feed leaves the reactor from an outlet in the reactor cap and reaches the GC (Inficon, Micro GC Fusion Gas Analyzer), which measures the product concentrations. Moreover, a pressure indicator is connected on the line from the reactor to the GC. The CO<sub>2</sub> cylinder is connected to a mass flow controller (Bronkhorst EL-FLOW model F-201CV), which regulates the flow rate of CO<sub>2</sub> fed to the reactor.

All that the possible leakages are averted with the GC: the reduction can occur when the presence of nitrogen is very low. The presence of nitrogen means that there are leakages in the reactor or in the connections. The reactor is then filled with the electrolyte solution (66 ml) and the solution is saturated with CO<sub>2</sub> by bubbling it into the liquid; the CO<sub>2</sub> indicator is used for checking when the gas dissolves.

It is used a solution of KOH for the blank, then it is compared with a solution that contains the Choline Glycine, the table 4.1 shows the molarity of solutions.

The software used shows the flow (ml/min) of gas bubbled and the temperature (K) thanks to a temperature indicator (TI in Fig. 4.1).

Table 4.1: The different solutions used.

Solution	Concentration	Volume
KOH (blank)	2 M	66 ml
KOH + ChoGly	0.1 M – 0.8 M	44 ml – 22 ml
ChoGly	0.8 M	66 ml

The figure 4.1 is the conceptual scheme of the setup and it shows that the connections interact among themselves.

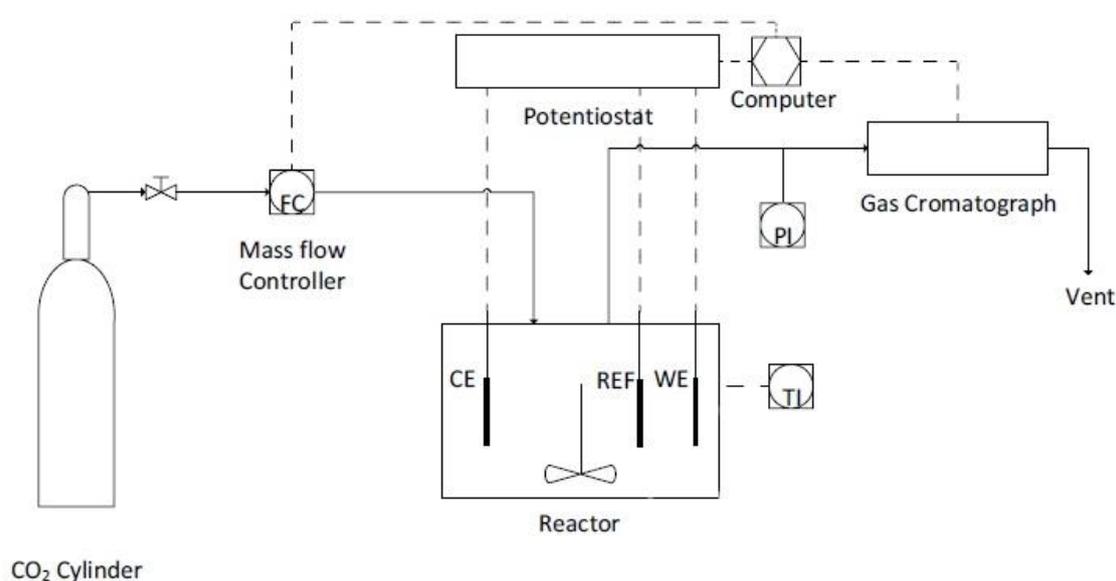


Figure 4.1: Conceptual scheme of the setup of CO<sub>2</sub> reduction.

Before all the tests, the GC has been firstly calibrated for CO, H<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub> and N<sub>2</sub>. In this part of the experimentation, the tests are mainly chronoamperometry analysis (measure of electrical current vs. time at constant potential) performed at three different potentials, for 90 minutes each applying different potentials in series as previously explained. This technique measures the resistance between the reference electrode and the cathode (mainly due to the electrolyte) and increases the potential applied to compensate the ohmic drop due to the solution resistance. The experiments were repeated for three different electrolytes.

Initially has been performed the experiments on the blank, with a solution of KOH and without ionic liquid. The solution has been examined from -1V to -1.5V. The table 4.2 shows the pH and the conductivity of the electrolyte in three different moments of the reduction: before and after carbon dioxide bubbling and after test. It has been measured with the multi-parameter Eutech PC, that it can measure pH, conductivity and temperature. Carbon dioxide is acid and the bubbling acidify the solution improving the stir.

It is proceeded with the use of novel solvents that were never used for electroreduction of CO<sub>2</sub>. Choline chloride [Cho][Gly] was chosen. A solution with [Cho][Gly] was used as electrolyte in the carbon dioxide reduction with silver as catalyst. It is expected to be a promising electrolyte for CO production, as this ionic liquid is great absorbent of CO<sub>2</sub>. For the tests, a mixture of KOH and [Cho][Gly] and a solution with only choline glycine (see the table 4.1) were used. The mixture has its properties. It is visible from tables 4.1 and 4.2 that the variation of pH was larger in the solution with ionic liquid than in the KOH blank solution. The carbon dioxide was better absorbed in the solvent that contains ionic liquid because the CO<sub>2</sub> gas acidify the solution, as it was expected due to the reaction of CO<sub>2</sub> with H<sub>2</sub>O to produce carbonic acid (H<sub>2</sub>CO<sub>3</sub>), which may loose protons (H<sup>+</sup>) to form carbonate (CO<sub>3</sub><sup>2-</sup>) and bicarbonate (HCO<sub>3</sub><sup>-</sup>) thus decreasing the pH. Therefore, the pH decreased more rapidly in the choline glycine solution than in the blank one, because of the presence of a major quantity of carbon dioxide.

**Table 4.2:** *Conductivity and pH values of solution of KOH 2M (blank)*

pH	Conductivity [mS/cm]	
13,4	146	fresh solution
10,29	103,49	after bubbling CO <sub>2</sub>
8,52	149,04	after test

**Table 4.3:** *Conductivity and pH values of solution of KOH 2M and [Cho][Gly] 0.8M*

pH	Conductivity [mS/cm]	
13.4	146.00	fresh solution
10.29	103.49	Solution after bubbling CO <sub>2</sub>
8.52	149.04	Solution after test (saturation)

Furthermore, the pH value obtained from a choline glycine solution in water are reported in the Table 4.4 for comparison, which shows the trend of pH variation from fresh solution and after bubbling the CO<sub>2</sub> gas.

It is evident that the choline glycine solution absorbed a higher quantity of carbon dioxide than mixture and blank solution. The trend of CO<sub>2</sub> adsorption observed was: KOH < KOH + [Cho][Gly] < [Cho][Gly].

**Table 4.4:** *Conductivity and pH values of solution [Cho][Gly] 0.8M*

pH	Conductivity [mS/cm]	
11,29	70,5	fresh solution
8,5	67,5	Solution after bubbling CO <sub>2</sub>
7,42	15,1	Solution after test (saturated solution)

It is evident that the choline glycine solution absorbed a major quantity of carbon dioxide then mixture and blank solution. The trend is: KOH < KOH + [Cho][Gly] < [Cho][Gly].

The difference between fresh solution and the solution after bubbling point us that the presence of CO<sub>2</sub> decreases the conductivity values, in other words the values are similar in choline glycine solution, instead in blank solution the difference is largest. This behaviour of conductivity shows an idea of how reduction happens.

#### 4.1 Data elaboration

It is proceeded with the elaboration of data. Data came from the potentiostat and from the GC. The row of data from potentiostat is more accurate than the data from GC, because we had electrical current data every second, but the GC needs more time for elaboration. Therefore, the data of current have been averaged. The principles of elaboration are explained in this section, and the table 4.5 shows the conditions used.

**Table 4.5:** *General conditions of system*

Area of catalyst [cm <sup>2</sup> ]	2,4
Room Temperature [K]	300-305
Atmospheric Pressure [atm]	1

The two setups slightly differ in the way of reporting the data and the final results are not expressed in the SI. Nevertheless, with the aim of a simpler explanation of the equations, the SI has been used in the present section.

The current density consists in the ratio of current and area of electrode (Equation 4.1).

$$j = \frac{I}{A} \quad (4.1)$$

Where:

$j$  [mA/m<sup>2</sup>] is the current density;

$I$  [mA] is the electric current;

$A$  [m<sup>2</sup>] is the surface of catalyst.

From the gas flow rate and the concentration, it is possible to calculate the production rate of H<sub>2</sub> and CO as follows (Equation 4.2 and Equation 4.3).

$$\dot{n}_{CO} = \frac{y_{CO} \cdot \dot{V} \cdot P}{R \cdot T \cdot A} \quad (4.2)$$

$$\dot{n}_{H2} = \frac{y_{H2} \cdot \dot{V} \cdot P}{R \cdot T \cdot A} \quad (4.3)$$

Where:

$\dot{n}$  ( $\frac{mol}{s \cdot m^2}$ ) is the production rates respectively of CO and H<sub>2</sub>. It is the molar flow rates per unit area;

$\dot{V}$  ( $\frac{m^3}{s}$ ) is the gas total volumetric flow rate;

$P$  (Pa) is the pressure;

$R$  ( $\frac{m^3 \cdot Pa}{mol \cdot K}$ ) is the gas constant;

$T$  (K) is the temperature;

$A$  (m<sup>2</sup>) is the electrode area.

Finally, by using the production rate and current density, the Faradaic Efficiency can be calculated as following (Equation 3.4 and 3.5)

$$FE_{CO} = \frac{\dot{n}_{CO} \cdot Z_{CO} \cdot F}{j} \cdot 100 \quad (4.4)$$

$$FE_{H2} = \frac{\dot{n}_{H2} \cdot Z_{H2} \cdot F}{j} \cdot 100 \quad (4.5)$$

Where:

$\dot{n}_{CO}$  and  $\dot{n}_{H2}$  ( $\frac{mol}{s \cdot m^2}$ ) are production rates respectively of CO and H<sub>2</sub>;

$Z_{CO}$  and  $Z_{H2}$  ( $\frac{mol \cdot e^-}{mol}$ ) are moles of electrons needed to form a mole respectively of CO and H<sub>2</sub>;

$F$  ( $\frac{C}{mol \cdot e^-}$ ) is the Faraday constant;

$j \left( \frac{A}{m^2} \right)$  is the current density.

To know  $Z$  values, it is sufficient to consider the two half-cell reactions. The value is equal to 2 in both cases (Equation 3.6 and 3.7)



## 5. Results and discussion

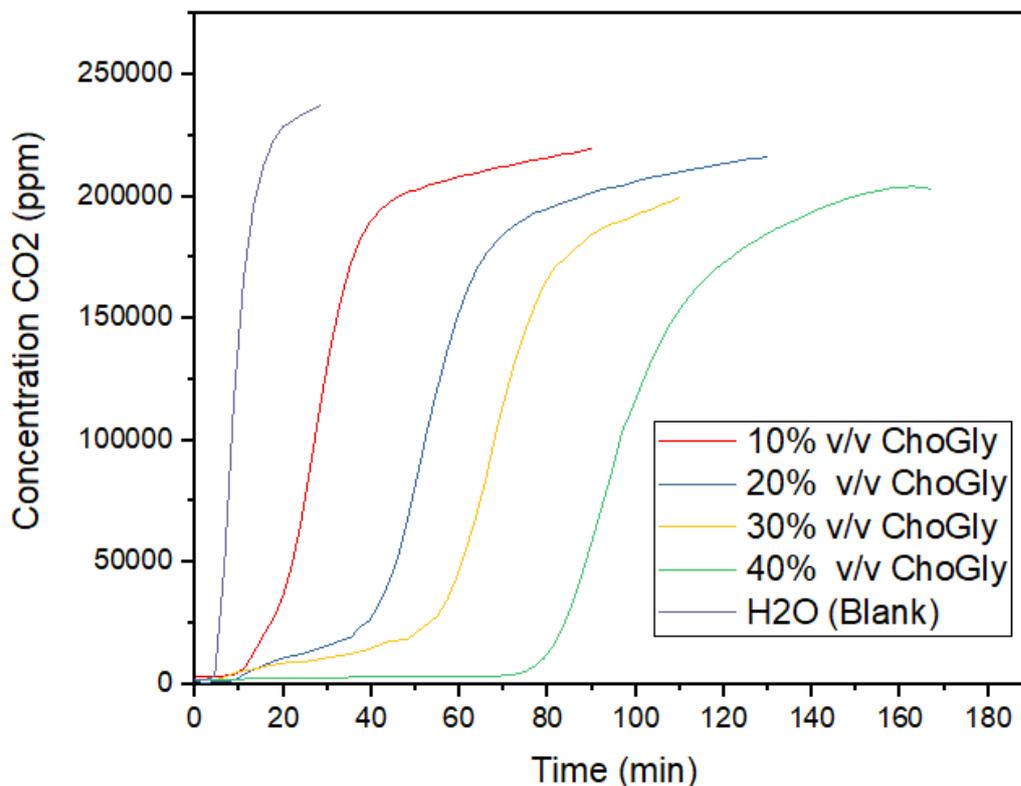
### 5.1 Absorption of CO<sub>2</sub> results

This section shows the results obtained from absorption tests. It has been shown that the IL, the Choline Glycine in the present case, increases the CO<sub>2</sub> absorption capacity as supported by literature [27, 48]. The solution that contains the IL shows higher capacity than the common solution, such as MEA, used in literature.

It has been modified various parameters to understand the behaviour of Choline Glycine solution. In the experiments there is a system delay owing to setup structure which has been corrected with measuring the break through point of CO<sub>2</sub> absorption in a blank solution of water.

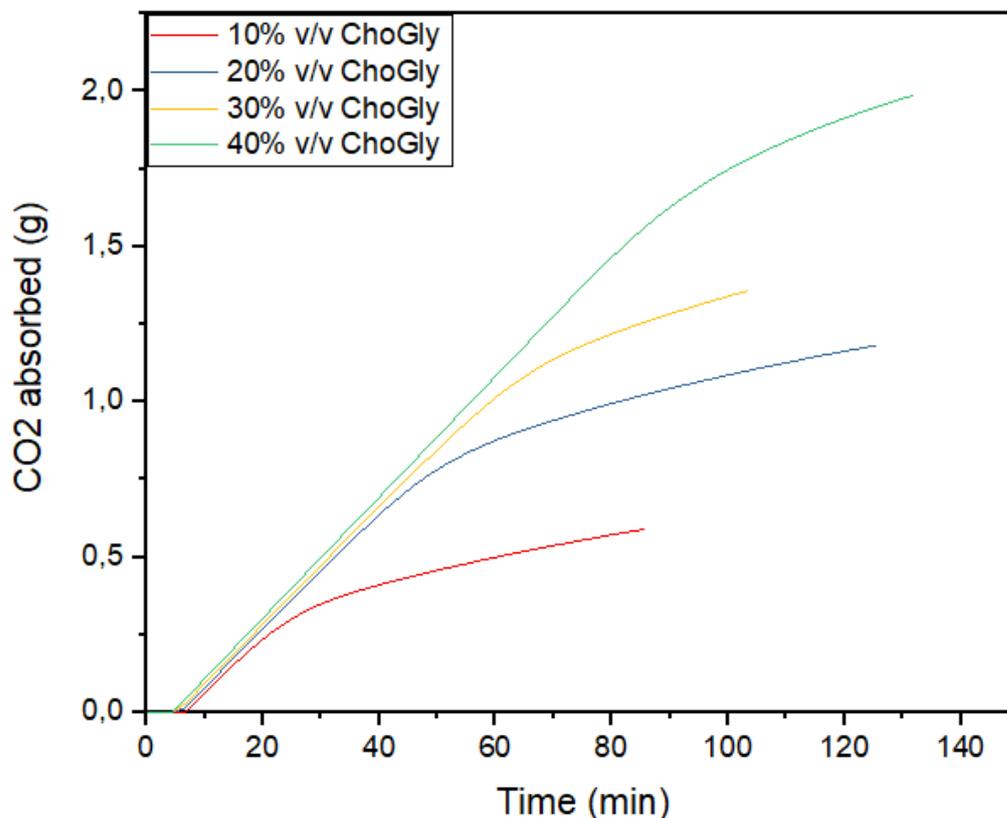
#### 5.1.1 Absorption tests for different Concentration of ChoGly at constant temperature of 24°C

The temperature of all the experiments are equal to 24°C. The figure 5.1 shows the concentration of CO<sub>2</sub> going out from the reactor vs time. The result for the blank solution of water is also shown in the figure. The blank solution has a CO<sub>2</sub> capacity absorption lower than the solution containing ChoGly. The absorption capacity increases with the increase in the concentration of ChoGly.



**Figure 5.1:** Concentration of CO<sub>2</sub> vs Time in solutions with different ChoGly concentrations.

The mass of absorbed CO<sub>2</sub> was calculated considering the response time of the system obtained by the break through curve for the blank solution of water and the solubility of CO<sub>2</sub> in the water. The Figure 5.2 illustrates the mass of CO<sub>2</sub> absorbed vs time.



**Figure 5.2:** CO<sub>2</sub> absorbed vs Time in solutions with different ChoGly concentrations.

The Table 5.1 reports the results of the amount of absorbed CO<sub>2</sub> and solvent capacity.

**Table 5.1:** Absorption capacity of CO<sub>2</sub> with different ChoGly concentrations

Concentration ChoGly v/v	Time [min]	CO <sub>2</sub> absorbed [mg]	CO <sub>2</sub> absorbed [mg/g IL]	CO <sub>2</sub> absorbed [mg/g solution]	CO <sub>2</sub> absorbed [mol/mol IL]
10 %	85.8	589.32	131.193	14.554	0.38
20 %	125.4	1181.13	131.470	28.819	0.400
30 %	103.4	1357.01	100.698	32.718	0.370
40 %	132.0	1987.82	110.631	47.365	0.337

It has been measured the weight of standard volume of the solutions, before and after the CO<sub>2</sub> bubbling, in order to measure the qualitative amount of absorption. The table 5.1 confirm that the absorption increases with concentration.

**Table 5.2:** *Qualitative absorption of CO<sub>2</sub> with different ChoGly concentrations*

Concentration v/v	Initial Weight of Solution [g]	Saturated Weight of Solution [g]	CO <sub>2</sub> absorbed [%]
10 %	10.1255	10.2008	0.8
20 %	10.1231	10.4629	3.36
30 %	10.2312	10.7059	4.70
40 %	10.4283	10.9562	5.16

### 5.1.2 *Absorption results for CO<sub>2</sub> capturing capacity of ChoGly at different operating temperatures*

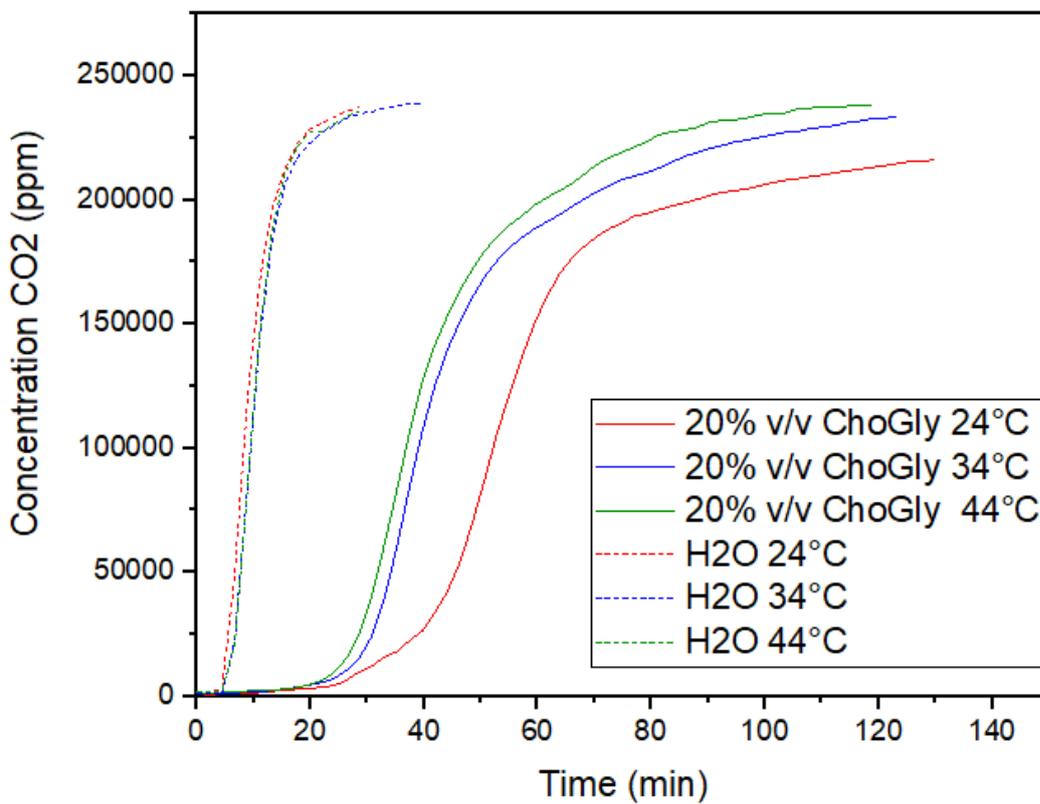
The results obtained with the variation of temperature are illustrate in the Figure 5.3. It has been chosen a solution of ChoGly (20% v/v) in water at different temperatures. This solution is compared with the blank solution at respective temperatures. The figure 5.3 shows that the absorption decreases with the increase of the temperature due to the exothermic nature of the reaction.

The figure 5.4 shows the absorbed mass of carbon dioxide vs time for the solution containing 20% v/v of ChoGly in water. It can be noted that the curves at 34°C and 44°C are similar to each other. The higher CO<sub>2</sub> absorption curve is belong to the breakthrough curve at room temperature. The curves of the figure 5.4 are obtained considering and subtracting their respective blank curve.

The Table 5.3 reports the results of absorption capacity of carbon dioxide into the solvent.

**Table 5.3:** Absorption capacity of CO<sub>2</sub> at different Temperatures in 20% v/v of ChoGly

Temperature [°C]	Time [min]	CO <sub>2</sub> absorbed [mg]	CO <sub>2</sub> absorbed [mg/g IL]	CO <sub>2</sub> absorbed [mg/g solution]	CO <sub>2</sub> absorbed [mol/mol IL]
24	125,4	1181,13	131,470	28,819	0,400
34	118,8	893,87	99,496	21,810	0,303
44	114,4	794,78	88,466	19,392	0,258



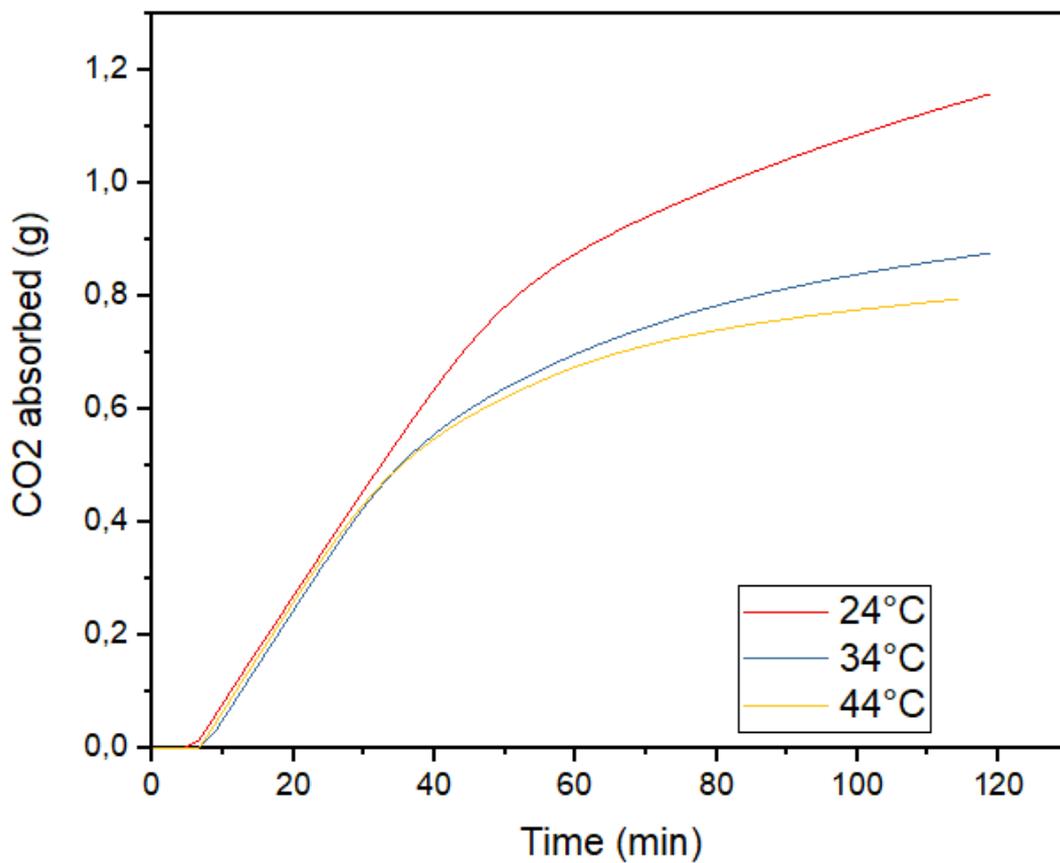
**Figure 5.3:** CO<sub>2</sub> absorbed vs Time in solution at different Temperatures

The table 5.4 reports the qualitative calculation of CO<sub>2</sub> absorbed in a solution with 20 % v/v of ChoGly in water at different temperatures.

**Table 5.4:** *Qualitative absorption of CO<sub>2</sub> in solution at different temperatures*

Temperature [°C]	Weight initial [g]	Weight finish [g]	CO <sub>2</sub> absorbed [%]
24	10.1231	10.4629	3.36
34	10.1231	10.4101	2.83
44	10.1231	10.3953	2.70

The table confirms the trend: the absorption reaction is not favoured at high temperatures.

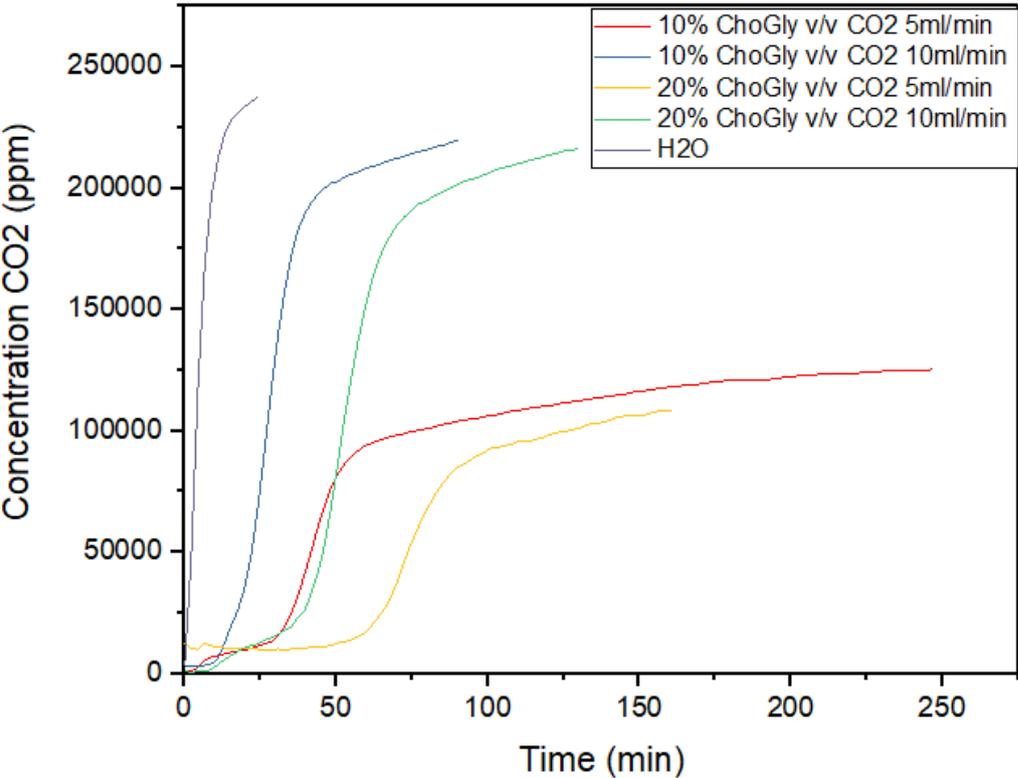


**Figure 5.4:** *CO<sub>2</sub> absorbed vs Time in solution of 20% v/v ChoGly at different Temperatures*

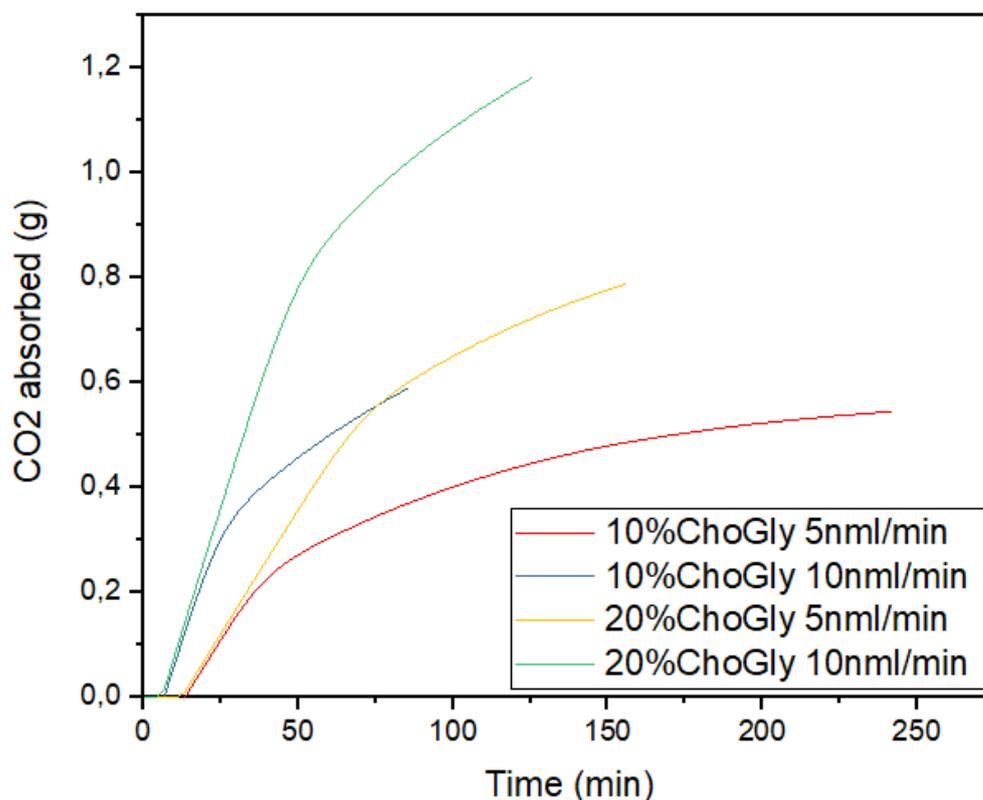
### 5.1.3 Absorption results for CO<sub>2</sub> absorption capacity of ChoGly for different Flow rate of inlet gas

It has been modified the ratio of CO<sub>2</sub> flow rate at constant temperature of 24°C. The Figure 5.5 shows the results of the experiment.

The results show that the system reaches equilibrium faster when the flow rate of the input flux is higher. in our case the CO<sub>2</sub> velocity of 10 ml/min. The figure 5.6 displays the absorbed mass of carbon dioxide vs time varying the flow rate. The table 5.5 presents the results of the absorption capacity of ChoGly as a function of input flow rate. Table 5.5 also shows an interesting solution behaviour that is viscosity influence over CO<sub>2</sub> absorption at lower flow rates. For instance. with a flow rates equal to 5 ml/min. CO<sub>2</sub> absorption is lower on the solution containing 20 % of IL rather than on the one containing 10 % of IL. With a flow rate of 10 ml/min. instead. CO<sub>2</sub> absorption is nearly the same.



**Figure 5.5:** Concentration of CO<sub>2</sub> vs Time in by varying the flow rate and ChoGly concentration of solution



**Figure 5.6:** *CO<sub>2</sub> absorbed vs Time varying the flow rate and ChoGly concentration of solution*

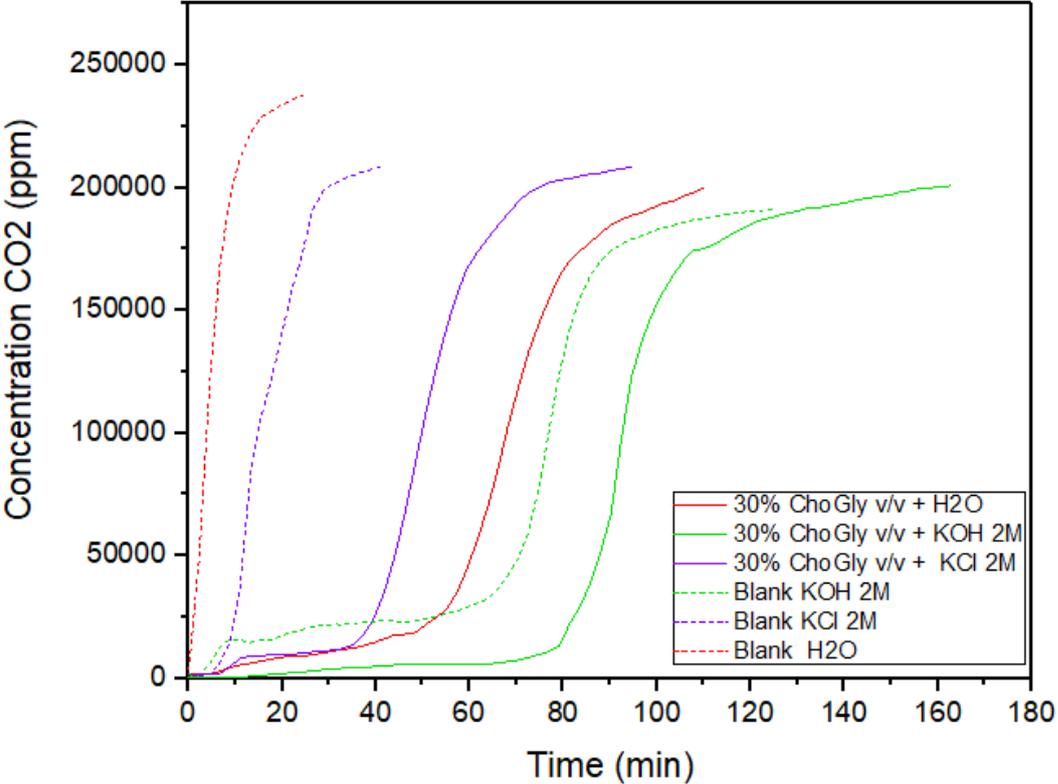
**Table 5.5:** *Absorption Capacity of CO<sub>2</sub> at different flow rate*

Flow rate [ml/min]	Concentration v/v	Time [min]	CO <sub>2</sub> absorbed [mg]	CO <sub>2</sub> absorbed [mg/g IL]	CO <sub>2</sub> absorbed [mg/g solution]	CO <sub>2</sub> absorbed [mol/mol IL]
5	10	242	544.44	121.202	13.446	0.458
5	20	156.2	788.55	87.772	19.240	0.267
10	10	85.8	589.32	131.193	14.554	0.380
10	20	125.4	1181.13	131.470	28.819	0.400

#### 5.1.4 Absorption results for CO<sub>2</sub> absorption capacity of ChoGly in different solution

It has been studied the effect of the IL or ChoGly in different solvents such as H<sub>2</sub>O, KOH and KCl. In this experiment the temperature is equal to 24°C and the concentration of ChoGly is equal to 30% (v/v solute/solvent). The figure 5.7 shows the concentration of CO<sub>2</sub> in the outlet of the reactor vs time with respective to the blank solution. The results show that the solution formed by KOH and ChoGly absorbs more CO<sub>2</sub> than the other solutions while the presence of ChoGly have more influence on the solution of ChoGly with H<sub>2</sub>O and KCl. As it can be

observed there is a bigger difference between the break through curve of blank solution of H<sub>2</sub>O and the break through curve of solution contained H<sub>2</sub>O and ChoGly.



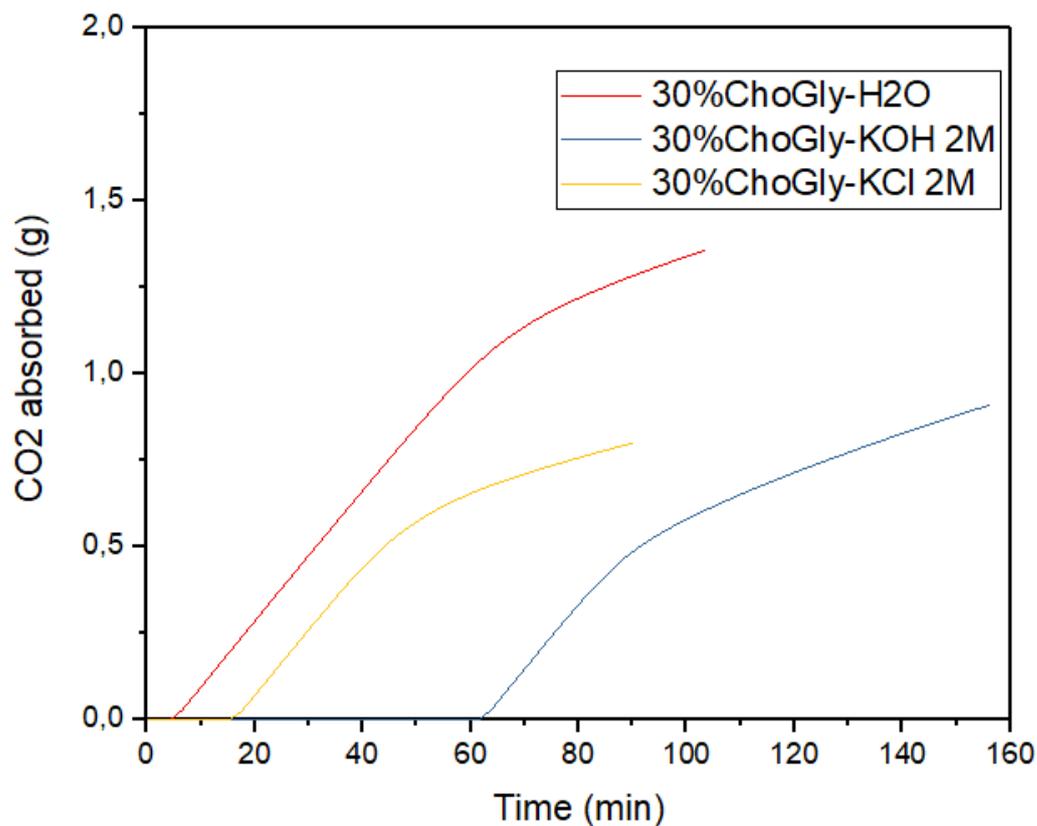
**Figure 5.7:** CO<sub>2</sub> absorbed vs Time in different solution

The figure 5.8 shows the amount of CO<sub>2</sub> absorbed vs time which is taking into consideration the respective effect of the blank solution. ChoGly seems to have more benefit in solutions with worst absorption capability.

The table 5.6 reports the results of absorption capacity calculation and table 5.7 reports the effect of blank solutions on CO<sub>2</sub> absorption capacity.

**Table 5.7:** CO<sub>2</sub> absorbed in Blank Solution

Solution	CO <sub>2</sub> absorbed [g]
KOH	1.7310
KCl	0.4491
H <sub>2</sub> O	0.1449



**Figure 5.8:** *CO<sub>2</sub> absorbed vs Time by varying solution*

**Table 5.6:** *Absorption Capacity of CO<sub>2</sub> in a solution with 30% v/v ChoGly varying solvent*

Solution	Time [min]	CO <sub>2</sub> absorbed [mg]	CO <sub>2</sub> absorbed [mg/g IL]	CO <sub>2</sub> absorbed [mg/g solution]	CO <sub>2</sub> absorbed [mol/mol IL]
KOH 2M	158.4	929.14	68.280	12.633	0.208
KCl 2M	90.2	800.22	59.381	11.611	0.181
H <sub>2</sub> O	103.4	1357.01	100.698	32.718	0.307

The table 5.8 reports the qualitative calculation of CO<sub>2</sub> absorbed and confirms the thesis.

**Table 5.8:** *CO<sub>2</sub> absorbed in Blank Solution*

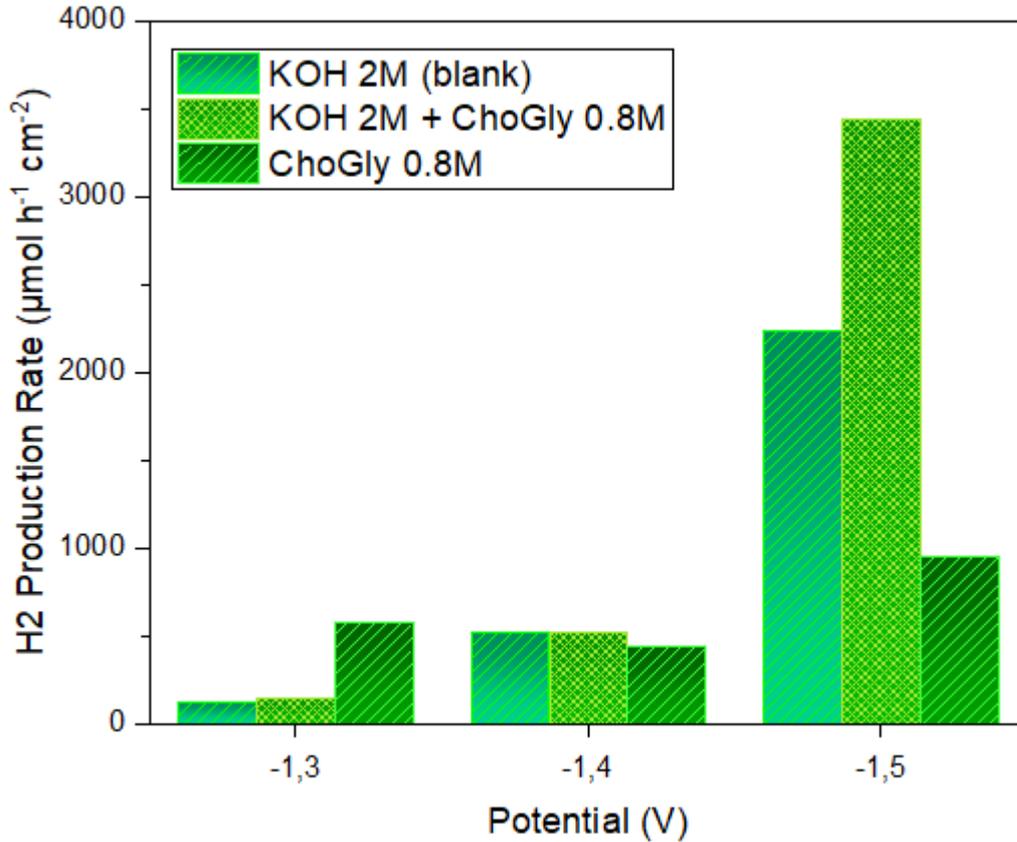
Solution	Initial Weight of Solution [g]	Saturated Weight of Solution [g]	CO <sub>2</sub> absorbed [%]
KOH	10.4591	11.0543	5.690
KCl	10.564	11.0536	4.634
H <sub>2</sub> O	10.2312	10.7059	4.639

## 5.2. *Electrocatalytic activity performance*

The effects of different electrolytes have been studied. The electroreduction of CO<sub>2</sub> can be a potential strategy for utilizing carbon dioxide as a carbon feedstock. In this work has been combined the important role of ILs. in particular the AAILs. with the electroreduction from CO<sub>2</sub> to CO on silver as catalyst.

It is observed that the solution of KOH 2M is the best solution for the CO<sub>2</sub> absorption. Therefore. this solution is considered as the blank solution for the electroreduction test. it is compared the results obtained from blank solution with the solutions containing choline glycine.

In Figure 5.9 we can note that the solution containing ChoGly increases the H<sub>2</sub> production rate and the respective Faraday efficiency. When the potential is equal to - 1.3V. it is evident that the solution of ChoGly without KOH has the higher H<sub>2</sub> production rate. Instead with the potential of - 1.4V and - 1.5V the solution of solution of KOH 2M and ChoGly 0.8M has the higher H<sub>2</sub> production rate.



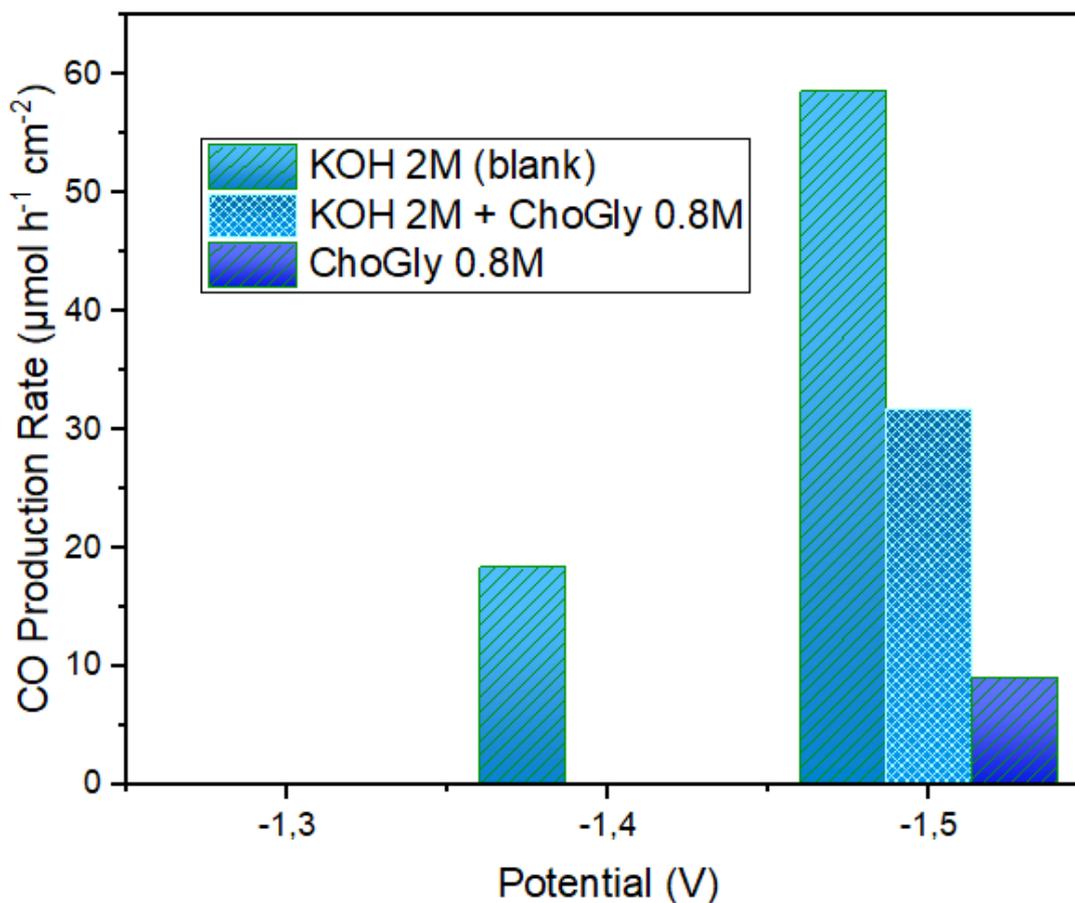
**Figure 5.9:** *H<sub>2</sub> production Rate at different potential and electrolytes*

Figure 5.10 shows CO production rate results. It can be noted that despite a better CO<sub>2</sub> absorption, ChoGly solution does not best fit for CO<sub>2</sub> conversion to CO as it lowers the blank solution production. In the blank solution it is seen CO production at - 1.4V and - 1.5V while in the solution containing ChoGly, CO production is evident only for potential equal to -1.5V.

The Table 5.9 shows the CO Faraday Efficiency in different tests.

**Table 5.9:** *CO Faraday Efficiency*

Solution	-1.3 V	-1.4 V	-1.5 V
KOH 2M	-	3.7	8.52
KOH 2M + ChoGly 0.8M	-	-	1.29
ChoGly 0.8M	-	-	1.50



**Figure 5.10:** *CO Production Rate at different potential in electrolytes*

The ChoGly solution work very well for CO<sub>2</sub> absorption, but it does not satisfy the expected results for the CO production. Higher potentials were not explored since the application of ionic liquid as an electrolyte should decrease the overpotential for the reaction and, therefore, this thesis work is focused on Ionic Liquid interactions at low potentials.

## 6. Conclusion

Carbon dioxide is an important greenhouse gas released through human activities, burning fossil fuels and deforestation. It is one of the greenhouse gases that have a high impact in Global warming. For this purpose. This thesis is focused on carbon dioxide absorption and its utilisation through the electrochemical reduction process into CO. To reach our goals, a novel ionic liquid, i.e. Choline Glycine, has been used. The conventional solvents used in industries are amine solutions. Instead, ionic liquids are a new generation of solvents that show promising properties in CO<sub>2</sub> absorption and in electrocatalysis. In this work, the ChoGly solution was used in an absorption process for capturing CO<sub>2</sub> and the same solution was used as an electrolyte in an electrochemical cell for reduction of CO<sub>2</sub> into CO.

In this work, it has been studied the absorption capacity of ChoGly solution with different concentrations of it in water, at different operating temperatures and with different electrolytes. From the performed absorption tests it was observed that the solution of ChoGly in 2M KOH solvent presented the highest absorption capacity.

By performing different tests at various temperature, we found that the ideal operating temperature for the absorption process was 24 °C. This is due to the exothermic nature of the absorption reaction of CO<sub>2</sub> with ChoGly and to the decrease of the CO<sub>2</sub> solubility at higher temperatures.

The second objective of this thesis is to evaluate the feasibility of the electrochemical reduction of CO<sub>2</sub> to CO by using the ChoGly solution as an electrolyte. It was assumed that a solution with highest absorption capacity for CO<sub>2</sub> could have the higher CO production rate as well.

The catalyst chosen for the reduction from CO<sub>2</sub> to CO was a silver foil, since it is a well-known catalyst for this reaction. From the electrochemical experiments, we have found that the ChoGly solution increased the H<sub>2</sub> production rate, while decreases the CO production rate. CO<sub>2</sub> electroreduction has already been achieved with some IL's but AAIL's were investigated for the first time for this purpose. From this work, it can be noted that they don't best fit for this objective apparently because the CO<sub>2</sub><sup>-</sup> radical formation reaction is thermodynamically disadvantaged. Another hypothesis is the transformation of ChoGly to a molecule able to co-catalyse the H<sub>2</sub> evolution reaction but capturing at the same time the CO<sub>2</sub>. However, the reversibility of that process should be investigated as well as the chemical transformation of the CO<sub>2</sub>-ChoGly formed compound.

Literature reviews done on electroreduction of CO<sub>2</sub> until today didn't study the properties of AAILs as a potential electrolyte. In this work, based on the results achieved, we observed that it is important to investigate the electroreduction potential of AAILs for CO<sub>2</sub> reducing purposes by using different catalysts. Analysis should be performed by using different types of AAILs than ChoGly. For instance, ChoAla, that is an alanine based AAIL, could be studied in order to compare the reactivity of another anionic group coupled to the Choline group. Further

investigations on AAIL could open the way to the use of sustainable ionic liquids not containing amino acid for the simultaneous capture and conversion of the CO<sub>2</sub>.

## 7. List of simbols

ILs	Ionic Liquids
AAILs	Amino Acid Ionic Liquids
ChoGly	Choline Glycine
[EMIM]	1-ethyl-3-methylimidazolium
[BIMIM]	1-butyl-3-methylimidazolium
ChoAla	Choline Alanine
GC	Gas Chromatograph
MEA	Mono-ethan-amine
AA	Amino acid
SHE	Standard Hydrogen Electrode



## 8. Reference

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