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Valorization of atmospheric carbon dioxide: from homogeneous to heterogeneous catalysts



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Riassunto

Introduzione

L'effetto serra è un fenomeno naturale di regolazione della temperatura terrestre e pertanto, il ruolo dei gas serra è quello di filtrare, assorbire e riflettere le radiazioni solari, garantendo una temperatura media del pianeta pari a 14 °C. L'atmosfera della Terra è composta soprattutto da azoto, ossigeno e argon e da una bassa percentuale di gas serra, che includono principalmente il biossido di carbonio (CO₂), il metano (CH₄) e l'ossido di diazoto (N₂O). La loro crescente concentrazione in atmosfera è causa del *global warming*, ovvero di un surriscaldamento della superficie terrestre che, a sua volta, comporta lo scioglimento dei ghiacciai, la perdita di biodiversità, l'innalzamento del livello dei mari, ecc. Ovvie misure preventive sono state prese per ridurre la concentrazione dei gas serra. Nel 1997, ad esempio, è stato sottoscritto dai Paesi industrializzati il Protocollo di Kyoto, l'accordo internazionale che sancisce una limitazione sulle emissioni di sei gas serra (biossido di carbonio (CO₂), metano (CH₄), ossido di diazoto (N₂O), esafluoro di zolfo (SF₆), perfluorocarburi (PFC) ed idrofluorocarburi (HFC)), tenendo in considerazione le condizioni di sviluppo dei Paesi aderenti. Tra quelli citati, il biossido di carbonio risulta avere una concentrazione atmosferica che cresce in maniera incontrollata. Esso è prodotto dai fenomeni di combustione associati ad attività antropiche e in particolare, da impianti di produzione di elettricità a combustibili fossili e dai trasporti, settori che ricoprono una percentuale del 79% in termini di emissioni di CO₂. Per ridurre la concentrazione di anidride carbonica antropica, sono disponibili due differenti strategie: *Carbon Capture and Storage (CCS)* e *Carbon Capture Utilization (CCU)*. Entrambe prevedono il recupero di CO₂ dagli effluenti gassosi degli impianti di combustione e a tale fase di cattura può seguire un immediato stoccaggio del gas serra o una conversione dello stesso in prodotti ad alto valore aggiunto. Il recupero della CO₂ dai gas di scarico può essere realizzato seguendo tre diverse soluzioni: post-combustione, cioè assorbimento mediante solvente dai gas esausti, pre-combustione, in cui il combustibile subisce una prima fase di gassificazione a basse concentrazioni di ossigeno, e l'ossi-combustione, in cui si utilizza ossigeno puro in camera di combustione. L'eventuale stoccaggio, previsto dalla CCS, avviene in siti di confinamento geologico, dotati di una certa porosità, un certo spessore ed una certa permeabilità per prevenire qualsiasi tipo di rischio ambientale. La trappola geologica viene scelta in modo tale da contenere il gas per un periodo di tempo dell'ordine di centinaia di anni e solitamente può essere un vecchio giacimento di idrocarburi, una falda acquifera salina oppure profondità oceaniche. La scelta di questa strada implica sicuramente costi elevati associati alla separazione, alla purificazione e al trasporto dell'anidride carbonica.

La CCU, invece, consiste nell'utilizzare e riciclare la CO₂, considerata come una risorsa, per la produzione di combustibili o composti chimici da impiegare in processi industriali su larga scala. La conversione dell'anidride carbonica può essere condotta attraverso metodi chimici oppure per riduzione fotochimica o elettrochimica della molecola. Il processo fotochimico simula la fotosintesi biologica dei vegetali sfruttando l'energia solare ed è, infatti, denominato "fotosintesi artificiale". Esso prevede tre step: assorbimento dell'energia luminosa, formazione della coppia elettrone-vacanze e trasferimento delle cariche in superficie dove avvengono i processi ossido-riduttivi. E' necessario che l'energia per foto-eccitare la superficie del semiconduttore, che funge da catalizzatore, sia di un valore superiore alla band gap del materiale così da poter separare le cariche. L'unica forza motrice per la conversione fotochimica è l'energia solare e non sono richieste particolari condizioni di temperatura e pressione. Altra alternativa per la valorizzazione della CO₂ è la riduzione elettrochimica, che presenta una serie di aspetti positivi. In primo luogo, i sistemi utilizzati sono modulari, compatti e adatti per una

scale-up ed inoltre, l'elettricità utilizzata nel processo può essere generata da fonti di energia alternative (energia geotermica, idroelettrica, eolica ecc.) che non presuppongono la formazione di ulteriore anidride carbonica. L'elettro-riduzione consta di un trasferimento di uno o più elettroni, che risulta essere non spontaneo vista l'elevata stabilità termodinamica della molecola. Le cinetiche di reazione, infatti, sono lente e i potenziali di riduzione richiesti per l'acquisto degli elettroni molto alti; in particolare, la grande barriera energetica da superare è quella dovuta alla formazione dell'intermedio di reazione $\bullet\text{CO}_2^-$, a cui è associato un potenziale di riduzione pari a - 1.9 V, valutato rispetto all'elettrodo di riferimento ad idrogeno (SHE) (pH= 7). Inoltre, nelle stesse condizioni di reazione, risulta favorita la produzione di idrogeno (H_2) a partire dalla riduzione dei protoni H^+ . Pertanto, è indispensabile l'impiego di un catalizzatore che ottimizzi le velocità di reazione, riduca i valori di potenziale richiesti per la formazione del radical anione e favorisca la riduzione di biossido di carbonio piuttosto che quella degli ioni idronio. Generalmente, i catalizzatori impiegati sono i metalli di transizione o i corrispondenti complessi metallici, in quanto tali elementi hanno la peculiarità di avere orbitali d semivuoti e risultano, pertanto, efficienti nel trasferimento elettronico. La corrente elettrica, fornita da una sorgente esterna, viene trasferita sotto forma di elettroni dal catodo al catalizzatore, il cui atomo metallico si riduce, per poi scambiare gli elettroni acquistati con la molecola di CO_2 . Il prodotto di reazione non è formato da un'unica specie, ma risulterà essere una miscela di composti dipendente dal tipo di catalizzatore impiegato e dal tipo di potenziale applicato. Altri fattori che influenzano la composizione della miscela in uscita sono le condizioni operative del sistema, il tipo di elettrolita e la forma e il materiale del catodo, cioè l'elettrodo in corrispondenza del quale avvengono le reazioni di ossidoriduzione. I possibili composti chimici prodotti sono il monossido di carbonio (CO), l'acido formico (HCOOH), l'etilene (C_2H_4), il metanolo (CH_3OH), il metano (CH_4) ecc. Essi possono essere valutati come materie prime per la sintesi di altri composti o possono essere convertiti in idrocarburi combustibili. Ad esempio, il monossido di carbonio è uno dei reagenti, insieme all'idrogeno, del processo chimico Fischer-Tropsch, finalizzato alla produzione di combustibili sintetici. Il metanolo, invece, può essere direttamente impiegato come combustibile nelle fuel cells o come *feedstock* per la produzione di formaldeide acetica, metil-t-butil etere (MTBE) e metacrilato di metile (MMA).

Catalisi omogenea ed eterogenea per la riduzione elettrochimica di CO_2

La riduzione elettrochimica della CO_2 può essere condotta in condizioni di catalisi omogenea oppure in condizioni di catalisi eterogenea.

Nel primo caso, il catalizzatore funge da ponte tra la molecola di biossido di carbonio e l'elettrodo, sostituendo così il diretto passaggio di elettroni tra l'elettrodo e il substrato, e la reazione di riduzione si innesca al potenziale di riduzione del catalizzatore. Le molecole di anidride carbonica e la specie catalitica si trovano nella stessa fase. In condizioni omogenee, il processo catalitico può avvenire secondo un trasferimento elettronico *outer-sphere* oppure un trasferimento elettronico *inner-sphere*. Il primo meccanismo prevede che il passaggio di elettroni si verifichi tra il catalizzatore in forma ridotta e il substrato, senza che essi reagiscano tra loro. Il trasferimento elettronico porta alla formazione del catalizzatore in forma ossidata e della specie radicalica $\bullet\text{CO}_2^-$. Il secondo meccanismo, invece, è assimilabile alla catalisi chimica, in quanto il catalizzatore ridotto e la CO_2 si combinano formando un intermedio di reazione e questo step è, poi, seguito dalla formazione del prodotto di reazione. Per la riduzione della molecola di biossido di carbonio si predilige l'attivazione chimica, così da evitare la formazione del radical anione, a cui è associata un'elevata riorganizzazione energetica. Tipicamente, il catalizzatore, il cui sito attivo è rappresentato dall'atomo metallico, è caratterizzato dal suo potenziale di riduzione e la corrispondente specie ridotta deve essere dotata di una certa stabilità. In fase omogenea, un buon elettro- catalizzatore dovrebbe operare

in condizioni simili a quelle del potenziale termodinamico di reazione e soprattutto con elevate velocità di reazione così da aumentare la resa del processo.

La riduzione elettrochimica eterogenea prevede che il catalizzatore sia presente in una fase diversa da quella del substrato, di solito in fase solida. Una prima possibile alternativa è scegliere un elettrodo tale da fungere esso stesso da elettro- catalizzatore e il processo si sviluppa in quattro passaggi: adsorbimento della molecola di CO_2 sulla superficie dell'elettrodo, trasferimento elettronico, riorganizzazione e desorbimento dei prodotti di reazione. Materiali come il platino, l'argento, lo zinco, il rame e il palladio e gli ossidi dei metalli di transizione, impiegati per la costruzione di elettrodi di lavoro, sono risultati efficienti per la riduzione elettrochimica del biossido di carbonio. La scelta del tipo di elettrodo determina la distribuzione dei prodotti di reazione, nonostante la selettività del materiale sia difficile da predire poiché dipende da numerosi fattori quali la temperatura, il tipo di solvente e di elettrolita di supporto, i difetti di superficie ecc. La seconda soluzione prevede di modificare la superficie dell'elettrodo, immobilizzando su di essa le molecole di complessi metallici organici. L'immobilizzazione può essere realizzata seguendo differenti approcci che prevedono la formazioni di legami covalenti e non tra le molecole di catalizzatore e gli atomi della superficie dell'elettrodo. Uno dei metodi è il *self- assembled monolayers* (SAMs) che consiste nel creare un monostrato organizzato di molecole in cui una delle estremità mostra affinità per la specie da ridurre. Questa tecnica è altamente riproducibile e facilmente applicabile, ma limitata dal tipo di materiale della superficie conduttiva. La tecnica di *diazonium electro- grafting*, invece, risulta più versatile sotto questo aspetto perché permette la costruzione di un strato stabile su diverse superfici conduttive; combinando uno step chimico con uno elettrochimico, il catalizzatore viene fissato covalentemente alla superficie elettrodica. Una soluzione più innovativa è rappresentata dall'utilizzo di strutture di nanotubi in carbonio. Le specie catalitiche possono modificare la superficie dell'elettrodo grazie al loro assorbimento fisico sulle strutture in carbonio, caratterizzate da una buona conduttività e da elevata area superficiale.

Attualmente, non è possibile stabilire se per la riduzione elettrochimica dell'anidride carbonica sia più favorevole l'elettrocatalisi omogenea o quella eterogenea. La fase di separazione dei prodotti e di riciclo del catalizzatore, per esempio, è più fattibile in condizioni eterogenee che in quelle omogenee. Questo aspetto della catalisi omogenea limita, infatti, la sua applicazione in processi industriali, sebbene essa sia caratterizzata da alta stabilità e selettività. I sistemi eterogenei, invece, visti i diversi tipi di siti attivi, sono dotati di bassa selettività ed inoltre, presentano problemi di diffusione poiché le reazioni avvengono in condizioni di mass-transfer. Un aspetto negativo che accomuna entrambi i tipi di catalisi è la facile degradazione del catalizzatore dovuta nei sistemi omogenei a reazioni indesiderate e in quelli eterogenei ad un avvelenamento dell'elettrodo causato soprattutto da impurità.

Complessi metallici usati per la conversione della CO_2 in CO

Il monossido di carbonio è una delle più importanti molecole da utilizzare per scopi industriali. E' necessario che un catalizzatore selettivo per la produzione di CO sia in grado di stabilire un legame forte con le molecole di monossido di carbonio e un legame debole con quelle dell'intermedio di reazione. Due classi di complessi metallici sono stati largamente studiati per la conversione di CO_2 in CO: i complessi porfirinici del ferro e del cobalto e i complessi polipiridinici a base di renio (Re), manganese (Mn), rutenio (Ru) e cobalto. Essi sono stati testati sia in fase omogenea che in quella eterogenea.

Per quanto riguarda il primo gruppo, Takahashi et al. hanno studiato l'attività catalitica di tre diverse strutture dei complessi porfirinici del ferro, dissolti in dimetilformammide. Essi hanno riportato elevate efficienze faradiche in termini di CO_2 , senza una significativa produzione di idrogeno. Per quanto riguarda questo gruppo di catalizzatori, lo sviluppo in termini di miglioramento della struttura dei leganti è notevole; infatti, Costentin et al. hanno dimostrato come velocizzare la reazione di riduzione modificando la struttura dei leganti. Inoltre, l'attività

catalitica di questi complessi è stata anche verificata e confermata in fase eterogenea, usando strutture di nanotubi in carbonio.

Il secondo gruppo di catalizzatori include i complessi metallici polipiridinici che hanno la caratteristica di accumulare elettroni sull'intera molecola e non solo sull'atomo metallico. Quelli che hanno riscontrato maggiore attenzione sono i complessi bipyridinici a base di renio, studiati per la prima volta nel 1980 da Lehn e Meyer. La formula chimica di questi catalizzatori è la seguente: $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$. La struttura bipyridinica del legante è stata nel tempo modificata e migliorata, fino ad arrivare alla classe di complessi, testati da Fontecave et al. in condizioni omogenee. La nuova famiglia di catalizzatori è indicata dalla seguente formula chimica: $[\text{Re}(\text{pyta})(\text{X})(\text{CO})_3]$ e $[\text{Re}(\text{tapy})(\text{X})(\text{CO})_3]$, dove per pyta si indica (4-(2-pyridyl)-1,2,3-triazolo) e per tapy (1-(2-pyridyl)-1,2,3-triazolo) e la cui struttura è riportata in Figura 1.12.

Il gruppo dei complessi pyta è stato l'oggetto di studio di questo progetto di tesi; in particolare, si è voluto investigare la possibilità di immobilizzare le molecole catalitiche sulla superficie di un elettrodo di carbonio vitreo, in cui le proprietà ceramiche e vetrose si combinano a quelle grafite.

Materiali e metodi

Preparazione e classificazione dei complessi Re/pyta

I catalizzatori studiati in questo progetto di tesi sono rappresentati dalla seguente formula chimica: $[\text{Re}(\text{pyta})(\text{Cl})(\text{CO})_3]$, (pyta: 4-(2-pyridil)-1,2,3-triazolo) e il loro processo di sintesi è riportato in Figura 2.1. Essi sono stati suddivisi in quattro classi a seconda del tipo di catena laterale che li caratterizza (Re/pyta-anilina, Re/pyta- N_3 , Re/pyta-pirene e Re/pyta-COOH), ed ogni classe è costituita, a sua volta, da complessi diversi tra loro per la lunghezza della catena laterale. Le strutture di ogni singolo catalizzatore sono riportate nelle Tabelle 2.1, 2.2, 2.3 e 2.4. Per ogni singola famiglia di complessi Re/pyta è stato previsto un differente metodo di immobilizzazione delle molecole sulla superficie dell'elettrodo di carbonio vitreo. I complessi Re/pyta-anilina sono immobilizzati tramite *diazonium electro-grafting* e *oxidative grafting*. Per i catalizzatori Re/pyta- N_3 , è stata sfruttata la combinazione di una reazione di *click chemistry* e della tecnica di *diazonium electro-grafting*. Per quanto riguarda i complessi Re/pyta-COOH e Re/pyta-pirene si è prevista un'immobilizzazione basata sull'uso di strutture di nanotubi di carbonio.

Tecniche elettrochimiche

Le tecniche elettrochimiche hanno permesso la caratterizzazione dei catalizzatori e lo studio della loro attività catalitica. In particolare, sono state utilizzate la voltammetria ciclica, l'elettrolisi a potenziale controllato e la cronoamperometria.

La voltammetria ciclica consente di studiare il processo di riduzione di un composto anche in assenza del substrato e consiste nel variare linearmente il potenziale dell'elettrodo di lavoro da un valore iniziale ad uno finale mantenendo costante la velocità di scansione. Questa tecnica è utile per determinare l'esatto valore del potenziale di riduzione del catalizzatore e per valutare la sua efficienza catalitica in presenza del substrato. I processi ossido-riduttivi hanno fisicamente luogo sulla superficie dell'elettrodo di lavoro e in accordo con la convenzione IUPAC, la reazione di riduzione si innesca in corrispondenza di potenziali negativi, al contrario per quella di ossidazione. Il trasferimento di carica può avvenire secondo un meccanismo faradico, in cui il passaggio di carica si verifica all'interfaccia elettrolita/elettrodo, o non faradico, che consiste in un adsorbimento/desorbimento sulla superficie elettrodo/elettrolita. Il grafico risultante da un esperimento di voltammetria ciclica è detto voltammogramma ed è caratterizzato dai seguenti parametri, indicati anche in Figura 2.2: picchi di potenziale catodico (E_{pc}) e anodico (E_{pa}), picchi di corrente catodica (i_{pc}) e anodica (i_{pa}). La Figura 2.3 riporta un esempio di voltammetria

ciclica condotta per lo studio di un catalizzatore per la riduzione di anidride carbonica. Conducendo l'esperimento in un sistema saturato con argon, è facilmente individuabile il valore del potenziale di riduzione del catalizzatore; alimentando CO₂, invece, è possibile valutare l'attività catalitica del composto confermata dalla presenza di corrente catalitica.

Nel nostro progetto di ricerca, gli esperimenti di voltammetria ciclica sono stati condotti in una classica cella elettrochimica a tre elettrodi usando un elettrodo di lavoro in carbonio vitreo con un diametro interno di 3 mm, un contro- elettrodo in platino e un elettrodo di riferimento in Ag/AgCl, separato dalla soluzione tramite un ponte salino. Un volume di 10 mL di acetonitrile ad una concentrazione di 0.1 M di TBAPF₆ (elettrolita di supporto) è stato saturato con Ar e CO₂ per 15 minuti prima dell'inizio dell'esperimento.

L'elettrolisi a potenziale controllato è una seconda tecnica elettrochimica che consente di valutare la selettività di un catalizzatore per la produzione di un dato composto. Essa consiste nel fissare il potenziale al valore del potenziale di riduzione del catalizzatore e nel valutare come la corrente vari nel tempo mantenendo il potenziale costante. L'elettrodo di lavoro impiegato per questo tipo di tecnica è dotato di un'area superficiale maggiore così da condurre l'esperimento per tempi più lunghi e da poter registrare valori di corrente più alti. L'elettrolisi è stata condotta in una cella elettrochimica costituita da due compartimenti, separati da una membrana porosa in ceramica. Nel compartimento catodico è stato inserito l'elettrodo di lavoro in carbonio vitreo con un diametro interno di 15 mm e l'elettrodo di riferimento in Ag/AgCl immerso in un ponte salino. Il compartimento anodico, invece, comprendeva l'elettrodo ausiliario in platino. Una soluzione di acetonitrile ad una concentrazione pari allo 0.1 M di TBAPF₆ è stata scelta come elettrolita per un volume di 7.5 mL nella parte catodica e di 4 mL in quella anodica. La soluzione è stata continuamente agitata durante l'esperimento per evitare la crescita dello spessore dello strato di diffusione. L'elettrolisi è stata eseguita per due ore, dopo aver saturato il sistema con un flusso gassoso di anidride carbonica.

La cronoamperometria, infine, prevede il monitoraggio della corrente nel tempo, applicando all'elettrodo una differenza di potenziale per un tempo sufficiente da far avvenire completamente la reazione elettrodica. Di solito, essa è utilizzata per lo studio di fenomeni di diffusione, assorbimento e per la valutazione di cinetiche chimiche.

Analisi chimiche

Durante gli esperimenti di elettrolisi, sono state monitorate la produzione di H₂ e di CO attraverso analisi condotte in gas cromatografi. Un campione di 50 µL di gas è stato prelevato ogni 30 minuti per valutare l'andamento delle reazioni. Inoltre, un campione di 100 µL di soluzione, diluito con acqua, è stato analizzato mediante cromatografia ionica così da rilevare la presenza di eventuali ioni in soluzione.

Metodi di immobilizzazione del catalizzatore

I metodi di immobilizzazione delle molecole di catalizzatore sulla superficie dell'elettrodo in carbonio vitreo si distinguono in due gruppi. Il primo gruppo comprende *diazonium electro-grafting*, *oxidative grafting* e immobilizzazione su strutture in nanotubi di carbonio modificati con gruppi amminici. Queste tecniche prevedono che le molecole del complesso metallico si leghino in maniera covalente alla superficie elettrodica. Il metodo di *diazonium electro-grafting* consta di un primo step chimico che porta alla formazione di un sale di diazonio e un secondo step, durante il quale il prodotto formato è legato per ossidazione elettrochimica alla superficie dell'elettrodo. Questa soluzione è stata sfruttata per il gruppo di complessi Re/pyta- anilina, essendo essi dotati del gruppo amminico NH₂, da cui formare il sale. La procedura di immobilizzazione consiste nel dissolvere il catalizzatore (0.5 mM) in una soluzione di 10 mL di ACN/ 0.1 M di TBAPF₆, aggiungendo 12 µL (nel caso dell'elettrodo con un diametro di 3 mm) di tert-butyl nitrito, come reagente dello step chimico condotto in assenza di luce. Il sistema è stato alimentato con Ar per 10 minuti. Successivamente, l'elettrodo, lavato con acqua ed

acetonitrile per rimuovere l'eventuale materiale non immobilizzato, è stato caratterizzato attraverso test di voltammetria ciclica, variando il potenziale tra + 0.4 V a - 0.6 V con una velocità di scansione di 20 mV/s. Per lo stesso gruppo di catalizzatori, è stata usata anche l'*oxidative grafting*, che si basa su una diretta ossidazione elettrochimica del gruppo amminico. Il catalizzatore è stato dissolto in un solvente anidro e un esperimento di cronoamperometria è stato condotto a + 1.3 V, ovvero al potenziale di ossidazione della specie catalitica. L'elettrodo è stato, poi, testato mediante voltammetria ciclica. L'immobilizzazione su strutture in nanotubi di carbonio con gruppi amminici ha interessato il catalizzatore Re/pyta- COOH. Le molecole del complesso sono fissate sulla superficie dell'elettrodo grazie al legame peptidico tra il gruppo carbossilico del catalizzatore e quello amminico delle strutture in nanotubi. La procedura prevede la preparazione di una sospensione di N- metil- 2-pirrolidone e di nanotubi con una concentrazione di 5 mg mL⁻¹, sottoposta ad un bagno ultrasonico per 30 minuti. Una goccia della stessa (2 µL per l'elettrodo di 3 mm di diametro) viene depositata sulla superficie dell'elettrodo, che viene, poi, posto in forno per 10 minuti per il processo di essiccazione. In ultimo, l'elettrodo con superficie modificata viene immerso in una soluzione di acetonitrile contenente il catalizzatore ad una concentrazione pari ad 1 mM, in assenza di luce e per 30 minuti così da facilitare l'immobilizzazione delle molecole di Re/pyta- COOH. La caratterizzazione dell'elettrodo è fatta tramite test di voltammetria ciclica.

Il secondo gruppo di tecniche, invece, si basa su metodi che permettono di legare le molecole catalitiche all'elettrodo attraverso legami non covalenti. Pertanto, si può sfruttare l'affinità fisica tra strutture di nanotubi in carbonio e l'unità poliaromatica dei complessi Re/pyta- pirene per immobilizzare questi ultimi via adsorbimento fisico. Anche in questo caso, è stata preparata una sospensione di nanotubi al carbonio ed N-metil-2-pirrolidone (5 mg mL⁻¹) che, previo bagno ultrasonico per 30 minuti, è stata depositata sulla superficie elettrodica (2 µL per l'elettrodo con diametro di 3 mm e 5 µL per l'elettrodo con diametro di 15 mm). Posto per 10 minuti nel forno, l'elettrodo modificato in carbonio vitreo è stato immerso in una soluzione di dimetilformammide con una concentrazione di catalizzatore pari a 1 mM, in assenza di luce e per 30 minuti. L'elettrodo, lavato con dimetilformammide e acetonitrile, è stato caratterizzato mediante voltammetria ciclica.

Risultati e discussione

Le classi dei Re/pyta- anilina e Re/pyta- pirene sono state testate sia in condizioni omogenee, dissolvendo i catalizzatori in soluzione, sia in condizioni eterogenee. Per i restanti gruppi, è stata valutata solo l'attività catalitica in fase omogenea, senza studiare ancora alcun tipo di metodo di immobilizzazione.

I complessi Re/pyta- anilina

I complessi C1, C2, C3 e C4 sono caratterizzati da un gruppo amminico legato all'anello benzenico e la differenza tra loro è dovuta alla lunghezza della catena laterale, come è facile osservare dalla tabella 3.1. Dissolvendo 0.5 mM di catalizzatore in una soluzione di ACN/0.1 M di TBAPF₆, è stata studiata la sua attività catalitica mediante voltammetria ciclica. Il potenziale è stato fatto variare tra + 0.5 V a - 2 V con una velocità di scansione pari a 100 mV s⁻¹. La scelta dell'acetonitrile come elettrolita è stata dettata dalla solubilità dei complessi a base di renio studiati e da una maggiore solubilità dell'anidride carbonica in esso rispetto che in acqua. Il set-up utilizzato è quello riportato in Figura 2.4. Il sistema è stato saturato in un primo momento con Ar e poi con biossido di carbonio. Le Figure 3.1, 3.2, 3.3 e 3.4 riportano i voltammogrammi di C1, C2, C3 e C4 rispettivamente. Osservando le curve blu, è facilmente visibile un primo picco di riduzione in corrispondenza di un valore di potenziale di - 1.45 V ed esso potrebbe essere associato alla riduzione del cloro. Un secondo picco di riduzione a potenziali più negativi

è dovuto alla riduzione della struttura legante del complesso e il valore di potenziale corrispondente è simile per ogni catalizzatore, nonostante la diversa lunghezza della catena laterale (- 1.66 V per C1, - 1.6 V per C2, - 1.68 V per C3 and - 1.7 V per C4). Quando il sistema è saturato con CO₂, per ogni singolo catalizzatore si registra una corrente catalitica osservabile dalle curve rosse delle Figure 3.1, 3.2, 3.3 e 3.4 e il catalizzatore che riporta il valore più negativo in termini di intensità di corrente è C1. Allargando la finestra di potenziale fino a valori positivi dello stesso, è possibile anche individuare i picchi di ossidazione dei complessi. La Figura 3.5, infatti, riporta il voltammogramma del catalizzatore C1 quando il sistema è saturato con argon e il potenziale è fatto variare tra - 2 V e + 2 V. Il primo picco a + 1.24 V è dovuto all'ossidazione del gruppo NH₂, il secondo picco in corrispondenza di + 1.48 V è associato all'ossidazione della coppia Re^I/ Re^{II} e l'ultimo, a + 1.93 V, è dovuto all'ossidazione della struttura legante. Inoltre, si è valutato anche l'effetto di un eventuale donatore di protoni da aggiungere in soluzione e si è visto che il trifluoroetanolo in una certa percentuale volumetrica potrebbe migliorare il processo di riduzione incrementando il valore di corrente catalitica.

I complessi Re/pyta- anilina sono stati immobilizzati sulla superficie elettrodica mediante *diazonium electro-grafting* e *oxidative grafting*. Seguendo la procedura spiegata nel paragrafo precedente, i catalizzatori, dopo uno step chimico, sono stati fissati sulla superficie dell'elettrodo in carbonio vitreo mediante voltammetria ciclica condotta in un range di potenziale tra + 0.4 V e - 0.6 V con una velocità di scansione di 20 mV s⁻¹ (Figura 3.7). L'unico picco di riduzione visibile è associato alla riduzione del sale di diazonio. I risultati riportati sono riferiti al catalizzatore C1, ma sono simili per C2, C3 e C4. Per confermare la funzionalità del metodo di immobilizzazione, l'elettrodo con superficie modificata è stato testato mediante voltammetria ciclica in una soluzione di ferrocianuro di potassio e il corrispondente voltammogramma è stato confrontato con quello di un *bare electrode*. In presenza di molecole immobilizzate sulla superficie, non è possibile vedere picchi di riduzione e di ossidazione associati al processo ossido-riduttivo del ferro (Fe^{III}/ Fe^{II}), che sono, invece, registrati nel caso in cui la superficie dell'elettrodo risulti accessibile (Figura 3.8). Successivamente, l'elettrodo è stato caratterizzato sempre mediante voltammetria ciclica in una soluzione di ACN/ 0.1 M di TBAPF₆, sia in un sistema saturato con Ar che in un sistema saturato con CO₂. In presenza di Ar, il picco di riduzione corrisponde allo stesso potenziale trovato in condizioni omogenee e integrando il voltammogramma di Figura 3.9, è stato possibile quantificare il numero di moli di molecole fissate sulla superficie elettrodica (l'ordine è nmol cm⁻²). Quando il sistema è saturato con anidride carbonica, il voltammogramma risultante ha registrato un picco di riduzione corrispondente ad un potenziale più positivo (- 1.4 V), ma una corrente catalitica minore (Figura 3.10). La presenza di molecole legate covalentemente sulla superficie dell'elettrodo è stata anche confermata conducendo esperimenti di voltammetria ciclica a diverse velocità di scansione dopo lo step di immobilizzazione. E' stato dimostrato un andamento lineare tra la corrente catodica e la velocità di scansione e ciò è segno che il sistema lavora in regime controllato dal fenomeno di assorbimento. Tuttavia, ripetendo l'esperimento nella soluzione di ferrocianuro di potassio, è sembrato che lo strato molecolare sia stato perso visto che il voltammogramma riporta picchi di ossidazione e riduzione associabili alle reazioni redox del ferro (Figura 3.12).

Lo studio della selettività dei catalizzatori in fase eterogenea e quindi l'eventuale produzione di CO è stata fatta attraverso l'elettrolisi a potenziale controllato. Il potenziale di elettrodo scelto è pari a - 1.7 V e cioè a quello di riduzione dei complessi catalitici. Le Figure 3.13 e 3.14 riportano l'andamento della corrente e della carica nel tempo. Per quanto riguarda l'intensità di corrente, essa risulta stabile durante le due ore di elettrolisi e tra C1, C2 e C3, il primo è quello che ha registrato una corrente più negativa. Infatti, attraverso analisi cromatografiche, si è visto che esso ha prodotto più CO rispetto agli altri, sebbene con una bassa selettività, in quanto ha favorito anche la reazione di produzione dell'idrogeno. Pertanto, C3 è risultato essere quello più selettivo, raggiungendo i valori più alti di efficienza faradica in termini di CO (EF= 47 %).

Inoltre, attraverso un esperimento di cronoamperometria condotto per 30 minuti ad un potenziale pari a + 1.3 V, il catalizzatore C1 è stato immobilizzato sulla superficie dell'elettrodo ossidando il suo gruppo amminico (*oxidative grafting*). I risultati ottenuti in questo caso sono assimilabili a quelli derivanti dal processo di *diazonium electro-grafting*. Poiché il voltammogramma di Figura 3.19, successivo alla fase di immobilizzazione, presenta la stessa forma di quello di Figura 3.9, si presuppone che lo strato molecolare immobilizzato sia uguale a prescindere dalla tecnica utilizzata. Gli stessi risultati non sono riproducibili per i complessi C2, C3 e C4.

I complessi Re/pyta- N₃

La struttura di questo gruppo di catalizzatori è riportata in Tabella 3.3 ed essi si differenziano tra loro per il numero di atomi di carbonio presenti nella catena laterale. Solubilizzati in una soluzione di ACN/ 0.1 M di TBAPF₆ ad una concentrazione di 0.5 mM, essi sono stati testati mediante voltammetria ciclica in un sistema saturato con argon e poi, con anidride carbonica. I catalizzatori hanno mostrato un picco di riduzione in corrispondenza dello stesso valore di potenziale (- 1.7 V) e il complesso che ha registrato una maggiore attività catalitica è stato il catalizzatore C7, a cui è associato il valore più negativo di corrente (Figura 3.30, 3.21, 3.22, 3.23). L'immobilizzazione di questi catalizzatori sulla superficie elettrodica potrebbe essere realizzata attraverso una combinazione di uno step di *click chemistry* e di *diazonium electro-grafting*.

Il complesso Re/pyta- COOH

Questo catalizzatore, la cui struttura è riportata in Tabella 3.4, è caratterizzato dalla presenza di un gruppo carbossilico. La sua attività catalitica è stata valutata solo in condizioni di catalisi omogenea e in presenza del biossido di carbonio, esso ha registrato elevati valori di corrente (Figura 3.24) e quindi ha mostrato una certa affinità per il processo di riduzione del gas. L'eventuale immobilizzazione sulla superficie dell'elettrodo in carbonio vitreo potrebbe essere condotta usando strutture di nanotubi in carbonio con gruppi amminici funzionali. In questo modo, sfruttando il legame peptidico tra il gruppo carbossilico e quello amminico, sarebbe possibile fissare covalentemente le molecole di catalizzatore sulla superficie elettrodica.

I complessi Re/pyta- pirene

A questa classe appartengono tre diversi tipi di catalizzatori caratterizzati dalla presenza di un gruppo poliaromatico (Tabella 3.5). La loro attività catalitica in fase omogenea è stata testata mediante esperimenti di voltammetria ciclica dissolvendo i complessi in una soluzione di dimetilformammide, vista la loro elevata solubilità in questo tipo di solvente. I voltammogrammi hanno riportato due diversi picchi di riduzione per VC-105 e VC-108 ed un unico picco per il complesso Py/3-33, in presenza di Ar. Alimentando un flusso di CO₂ al sistema, il valore più negativo di corrente è stato registrato per il catalizzatore VC-108.

L'uso di strutture di nanotubi in carbonio ha permesso di immobilizzare questo gruppo di complessi a base di renio attraverso adsorbimento fisico. Seguendo la procedura spiegata nella sezione precedente, le strutture di nanotubi sono state fissate sulla superficie elettrodica incrementandone l'area superficiale e l'elettrodo è stato, poi, caratterizzato attraverso voltammetria ciclica. Ciò è facilmente visibile comparando i voltammogrammi dell'elettrodo modificato e di un *bare electrode*; infatti, osservando le Figure 3.32 e 3.33, la corrente capacitiva registrata nel caso dell'elettrodo modificato è molto più elevata rispetto a quella di un *bare electrode*. Successivamente, i catalizzatori sono stati fissati sulla superficie dei nanotubi grazie all'adsorbimento del gruppo poliaromatico. Gli esperimenti di voltammetria ciclica hanno riportato uno spostamento del potenziale di riduzione dei complessi verso valori più positivi.

In seguito all'immobilizzazione dei catalizzatori sull'elettrodo di carbonio vitreo con diametro di 15 nm, i test elettrochimici di elettrolisi a potenziale controllato hanno consentito anche una

valutazione della selettività dei complessi. L'elettrolisi è stata condotta per due ore e ad un potenziale di elettrodo pari a - 1.7 V e saturando il sistema con anidride carbonica. Le Figure 3.37 e 3.38 riportano rispettivamente l'andamento della corrente e della carica sul tempo. La migliore performance in termini di riduzione della CO₂ è attribuita al complesso Py/3-33. Esso ha registrato, durante l'elettrolisi, il valore di intensità di corrente più negativo (- 250 µA) se confrontato con quello di VC-105 e VC-108. Dalle analisi cromatografiche effettuate, si evince che Py/3-33 ha prodotto la maggior quantità di CO e una bassa percentuale di idrogeno, nonostante sia risultato essere più lento rispetto a VC-105. Infatti, Py/3-33 ha iniziato a produrre monossido di carbonio solo dopo 30 minuti dall'inizio dell'elettrolisi. VC-105 ha prodotto monossido di carbonio fin dall'inizio dell'esperimento elettrochimico, ma contemporaneamente ha favorito anche la reazione di formazione dell'idrogeno. VC-108, invece, che ha riportato buoni risultati in condizioni omogenee, ha fornito la minor quantità di CO, come mostra la Tabella 3.6.

Conclusioni

L'interesse per lo sviluppo e lo studio di catalizzatori per la riduzione elettrochimica dell'anidride carbonica è in continua crescita in quanto finalizzato non solo alla diminuzione di biossido di carbonio atmosferico ma anche alla produzione di composti chimici ad alto valore aggiunto. Per quanto concerne la produzione di monossido di carbonio, molti catalizzatori sono stati esaminati in condizioni omogenee e solo pochi esempi sono relativi allo studio in fase eterogenea. La finalità di questo progetto di tesi è stata l'analisi di nuovi complessi polipiridinici a base di renio per convertire il biossido di carbonio in CO. Essi sono stati testati in fase eterogenea attraverso tecniche di immobilizzazione delle molecole catalitiche sulla superficie di un elettrodo in carbonio vitreo.

Dai risultati ottenuti si evince che, tra i catalizzatori del gruppo Re/pyta- anilina, C1, con la più corta catena laterale, è quello che ha registrato una corrente catalitica più negativa in condizioni omogenee ed in fase eterogenea ha prodotto più CO rispetto a C2 e C3. Tuttavia, C3 è risultato essere molto più selettivo rispetto a C1, in quanto non ha favorito la formazione di idrogeno e pertanto, ha raggiunto il più alto valore di efficienza Faradica in termini di moli di monossido di carbonio. Per quanto concerne l'altra classe di catalizzatori esaminata, Re/pyta- pirene, la migliore performance è stata ottenuta con il catalizzatore Py/3-33, caratterizzato dalla catena laterale più lunga. Py/3-33 ha esibito una buona attività catalitica e una buona selettività per la produzione di CO, nonostante sia risultato essere più lento rispetto a VC-105 e VC-108. In conclusione, il lavoro di tesi svolto lascia dei primi presupposti per ricerche future. Le prove effettuate hanno sicuramente confermato la funzionalità e la validità dei metodi di deposizione utilizzati, sebbene i parametri operativi, quali concentrazione del catalizzatore, solvente, tempo di permanenza, potenziale di lavoro, debbano essere mod per ottenere la combinazione ottimale. Studi più approfonditi dovrebbero essere condotti in merito agli altri metodi di immobilizzazione (*oxidative grafting*, *click chemistry/diazonium eletro-grafting* e *carbon nanotubes immobilization by a peptide coupling*). La tecnica di *oxidative grafting*, basata sul processo ossidativo del gruppo NH₂ (gruppo terminale dei complessi C1, C2 e C3), dovrebbe essere meglio esaminata per i complessi C2 e C3, magari considerando una previa neutralizzazione degli stessi. Inoltre, la combinazione di *click chemistry* e *diazonium electro-grafting* potrebbe essere una buona soluzione per legare covalentemente i catalizzatori del gruppo Re/pyta- N₃ alla superficie dell'elettrodo. Infine, il catalizzatore Re/pyta- COOH, che ha mostrato attività catalitica in condizioni omogenee, potrebbe essere immobilizzato e potrebbe modificare la superficie dell'elettrodo in carbonio vitreo attraverso un legame peptidico tra il gruppo carbossilico e il gruppo amminico delle strutture di nanotubi di carbonio.¹

1. Introduction

1.1 Carbon dioxide as Greenhouse gas and ways to valorize it: artificial photosynthesis

Earth's atmosphere is mostly composed of nitrogen, oxygen and argon. However, there is a small amount represented by greenhouse gases (0,1 % of total dry air). Greenhouse gases include carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and they have a great impact on Earth's temperature. In fact, solar energy hits our planet and a part of radiations are reflected by Earth's surface and another part is adsorbed warming our planet. When the Earth starts warming, infrared radiations are emitted and a part of them is adsorbed and re-emitted by greenhouse gases increasing the Earth's temperature (Figure 1.1). This process is necessary to keep warm the planet but an excessive amount of greenhouse gases can lead to an overheating of Earth's atmosphere. Global warming and its consequent climate change is one of most important problem in the world. For this reason in 1997 Kyoto Protocol was signed [1].

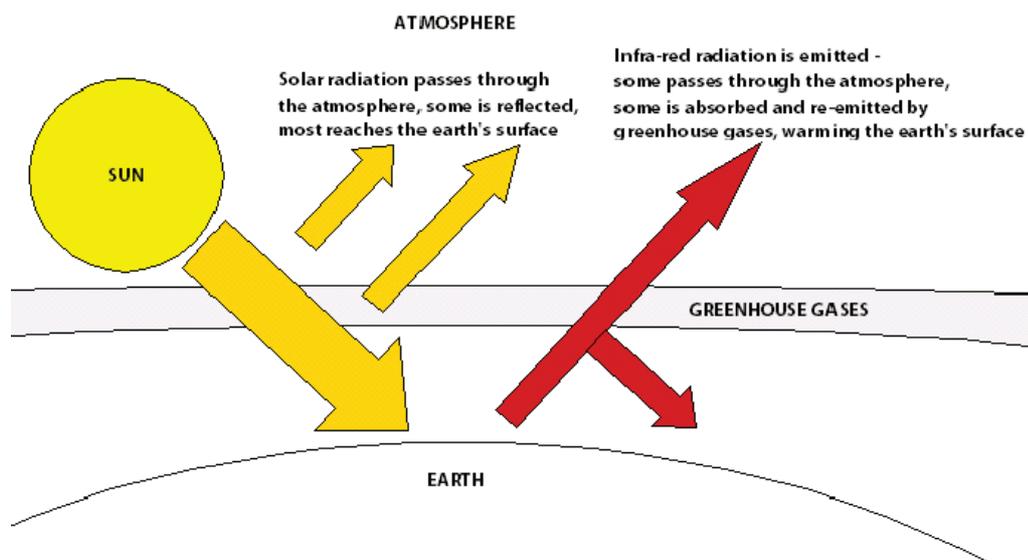


Figure 1.1: Greenhouse gas effect [1].

Kyoto Protocol is an agreement signed by industrialized countries that establishes limits for greenhouse gases emissions and different commitments for each developed country according to their economic development. It addresses six main greenhouse gases (carbon dioxide, methane, nitrous oxide, sulphur hexafluoride, hydrofluorocarbons and perfluorocarbons) [1]. In particular, CO_2 is the main greenhouse gas whose concentration is continuously growing, as it can clearly see in Figure 1.2.

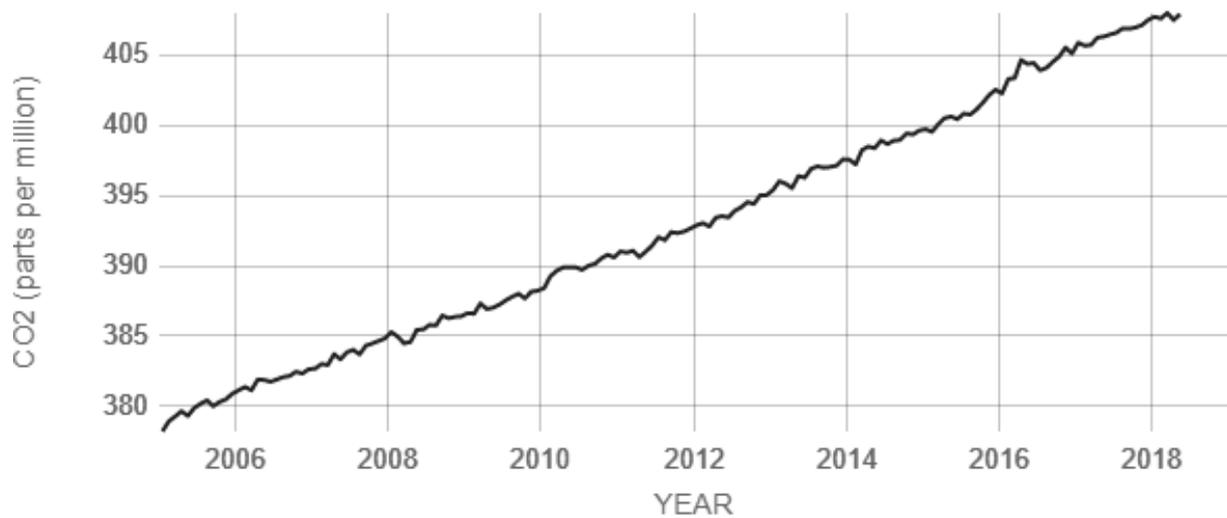


Figure 1.2: Carbon dioxide concentration in the atmosphere [31].

Production of carbon dioxide is mostly due to combustion phenomena associated with human activities as transportation, industrial processes and agriculture. In Figure 1.3 it is reported the CO₂ emissions by sector. A very big slice is represented by fuel combustion and fugitive emissions (79%). The other sectors cover just a small amount compared to fuel combustion (21%). The main source of carbon dioxide emissions comes from fuel combustion and fugitive emissions. High concentration of CO₂ due to fuel combustion comes from oil and gas-fired power stations producing electricity and road transportation, which consists of cars and collective passenger road transport. Other contributors of fuel combustion are manufacturing industries and households [1].

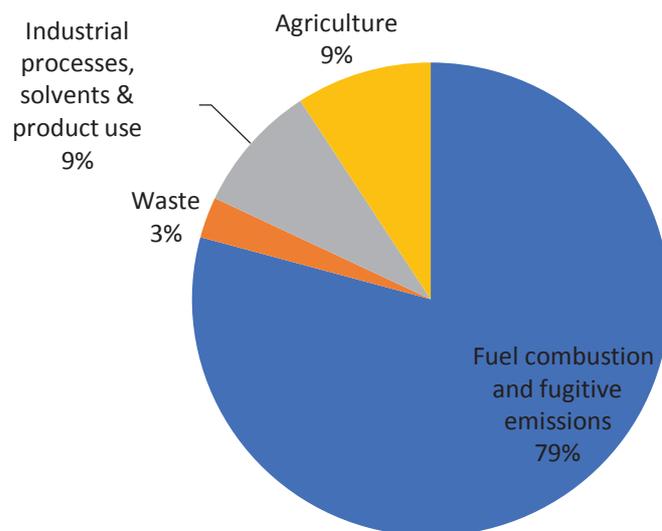


Figure 1.3: Total CO₂ emissions by sector [1].

Decreasing CO₂ production is mandatory to reduce global warming. At this day and age, a lot of strategies have been investigated and two main paths have been developed. One route can be to geologically sequester CO₂ and another is its conversion. Both of them involve carbon dioxide capture. To capture CO₂ three ways can be followed as indicated in Figure 1.4; one way is to recover CO₂ from exhaust gases, deriving from combustion processes, utilizing adsorption with a solvent. This method is called post-combustion and its main challenge for post-combustion CO₂ capture is its large load. In combustion exhaust gases, CO₂ level is usually low; therefore, the energy and associated costs for the capture unit to reach CO₂ concentration needed for transport and storage (above 95.5%) are high. A current study demonstrated that electricity costs could increase by 32% and 65% for post-combustion in gas and coal-fired plants. Another capture solution consists of a pre-combustion where the fuel, coal or natural gas, is pretreated before being burned. For coal, pretreatment step is a gasification under low oxygen level forming a syngas (a mix of CO and H₂). Successively, carbon monoxide can react with steam forming H₂ and CO₂. The carbon dioxide deriving from water gas shift reaction is easy to separate because of its high concentration in fuel gas mixture. However, pre-combustion process involves temperature associated heat transfer problem, high parasitic power requirement for sorbent regeneration and high costs for sorption systems. The last approach is oxy-fuel combustion where oxygen, instead of air, is used for combustion reducing nitrogen amount in exhaust gases. Using pure oxygen for the combustion, the flue-gas is mostly composed of CO₂, water, particulates and SO₂. Electrostatic precipitator and flue-gas desulphurization methods can remove particulate and SO₂, while the remaining gas with high CO₂ concentration can be compressed, transported and stored. The main disadvantage of this process is the high cost and the energy penalty for air separation unit because of the large amount of oxygen consumed [2].

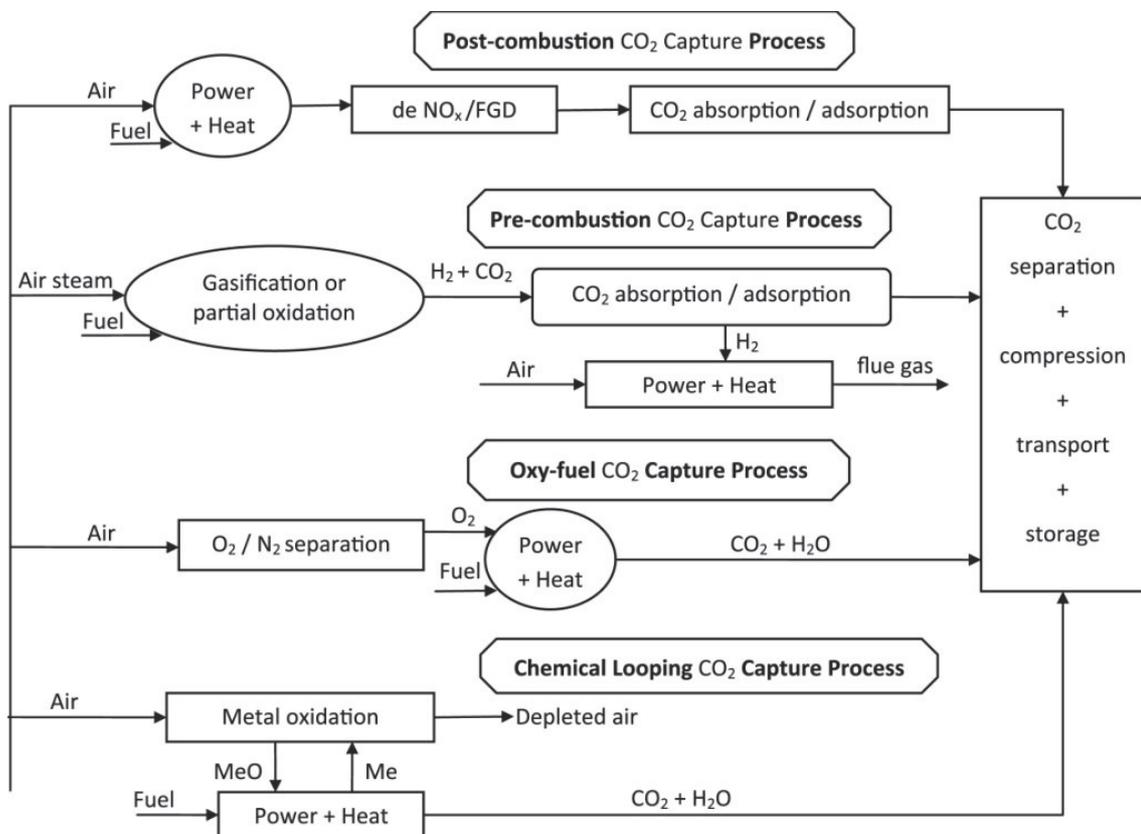


Figure 1.4: CO₂ capture technologies [2].

After capture, carbon dioxide stream can be transported for geological storage or for CO₂ utilization. Geological spots are usually used for CO₂ storage because, they can trap several tens of millions tons of carbon dioxide. The requirements for geological storage of carbon dioxide include appropriate porosity, thickness and permeability of the reservoir rock and a stable geological environment. The gases can be injected in depleted oil and gas reservoirs, coal beds, saline aquifers and deep Ocean [2]. However this route has a relevant environment impact and high costs deriving from CO₂ separation, purification and transportation.

On the other side, CO₂ conversion approach is able to produce renewable energies used into chemical field and chemical products with an high added value. Generally, carbon dioxide conversion can be performed by chemical methods, by electrochemical and photochemical reduction.

Photochemical reduction simulates biological photosynthesis and it uses solar energy to convert CO₂ into higher-energy products. It consists of three main steps (as shown in Figure 1.5). The first one is adsorption of photons from light radiation with the generation of charge carriers (electron-hole pairs). Charge carriers are separated transported and then, chemical reactions happen between species on the surface and charge carriers. Thanks to photoexcitation (photons energy should be equal or greater than the band gap of the semiconductor), the redox reaction begins and electrons go from the valence band (the highest energy band occupied by electrons) to the conduction band (the lowest energy band occupied by electrons). Photochemical conversion of CO₂ does not require high energy input, high temperature or high pressure conditions, as other methods, but only solar irradiation. [3].

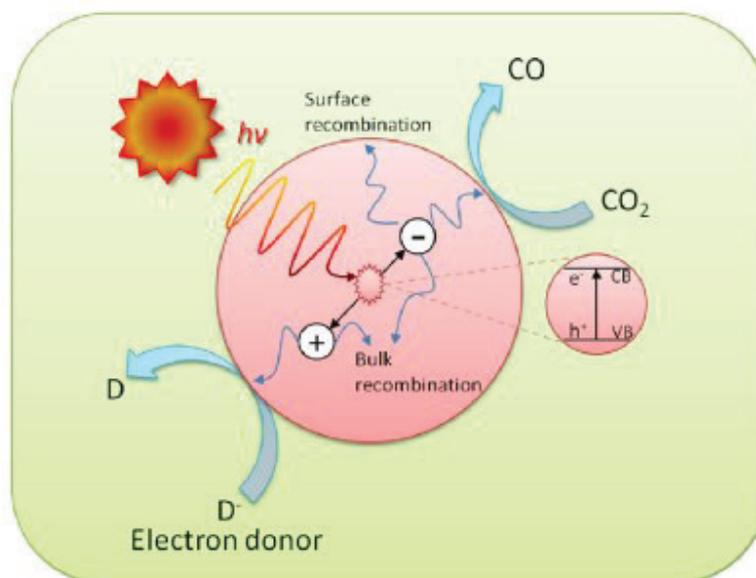


Figure 1.5: Schematic diagram of photo-excitation and electron transfer process [3].

An alternative pathway could be represented by electrochemical reduction of CO₂. In fact, this solution shows some advantages, as easy development due to the fact that it is modular, compact and easy for a scale-up. Another positive aspect is the fact that the process can be driven using different energy sources to produce electricity without generating any new CO₂ (for example: wind, hydroelectric, geothermal, tidal and thermoelectric processes) [4]. The main disadvantage is that the process, involving one or more electrons transfer, is not spontaneous because of the thermodynamic stability of the CO₂ molecule. Moreover, the kinetics is very slow and the reduction potential (it measures the capability of chemical species to gain

electrons) requested is very high. Therefore, to improve CO₂ conversion via electrochemical way, a high energy efficiency and high reaction rate are needed. As shown in Figure 1.6, the first barrier is the formation of a $\cdot\text{CO}_2^-$ radical anion. The high overpotential is due to this step which requires a standard potential equal to -1.9 V versus the standard hydrogen electrode (SHE). In addition, there is a competitive reaction: the hydrogen formation at cathode from proton reduction [5]. A possible solution is, for sure, the employment of a catalyst which could improve radical anion formation reducing the potential and can be selective for CO₂ reduction.

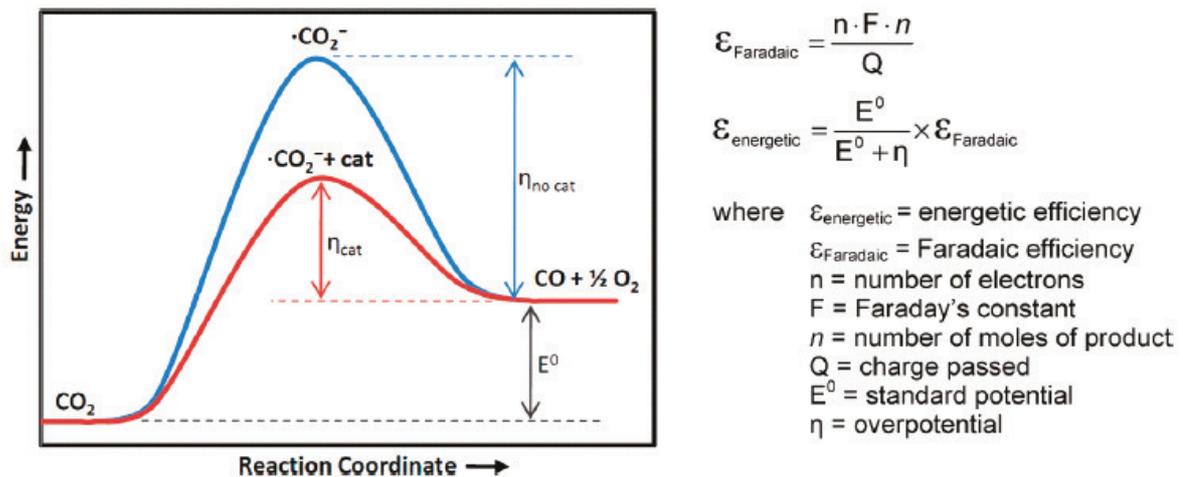


Figure 1.6: Qualitative reaction scheme for carbon dioxide conversion [5].

Generally, electro-catalysts for carbon dioxide reduction are transition metal elements and their associated complexes, as metal complex. They have vacant orbitals and active d electrons, which are able to energetically facilitate the bonding between the metal and the CO₂ [4]. The mechanism for the electro-reduction of CO₂ in presence of a catalyst is showed in Figure 1.7. The first step is the exchange of one or more electrons from the electrode to the metal atom and then from the metal atom to CO₂ molecule, leading to the carbon dioxide reduction.

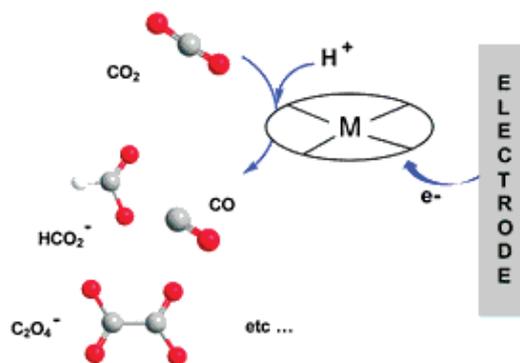


Figure 1.7: Mechanism of electro-reduction of CO₂ catalyzed from Catalysis of the electrochemical reduction of carbon dioxide [6].

The major products from the CO₂ electrochemical reduction with their corresponding potentials are showed in Table 1.1. Furthermore, electro-reduction product is not a single species, but a mixture containing several compounds, depending on the kind and selectivity of electro-catalyst

and potential applied [4]. The distribution of products depends on many factors such as operational conditions, type of electrolyte and form/type of material used as cathode. Some of products such as formic acid, carbon monoxide, ethylene, methanol and methane can be used as feed-stocks for chemical synthesis or converted into hydrocarbon fuels [7]. For example, carbon monoxide could be useful for chemical uses. In particular, in the Fischer-Tropsch process with H₂ (water electrolysis, WGS) CO is able to produce synthetic fuels or to produce other chemical compounds [8]. Another valuable product is methanol which could be directly used as a fuel in fuel cells or as a feedstock of many chemicals like formaldehyde acetic acid and the manufacture of methyl tertiary-butyl ether (MTBE) and methyl methacrylate (MMA) [9].

Half-electrochemical thermodynamic reactions	Electrode potentials (V vs. SHE) under standard conditions
$\text{CO}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- = \text{C}(\text{s}) + 2\text{H}_2\text{O}(\text{l})$	0.210
$\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- = \text{C}(\text{s}) + 4\text{OH}^-$	-0.627
$\text{CO}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^- = \text{HCOOH}(\text{l})$	-0.250
$\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- = \text{HCOO}^-(\text{aq}) + \text{OH}^-$	-1.078
$\text{CO}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^- = \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{l})$	-0.106
$\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- = \text{CO}(\text{g}) + 2\text{OH}^-$	-0.934
$\text{CO}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- = \text{CH}_2\text{O}(\text{l}) + \text{H}_2\text{O}(\text{l})$	-0.070
$\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l}) + 4\text{e}^- = \text{CH}_2\text{O}(\text{l}) + 4\text{OH}^-$	-0.898
$\text{CO}_2(\text{g}) + 6\text{H}^+ + 6\text{e}^- = \text{CH}_3\text{OH}(\text{l}) + \text{H}_2\text{O}(\text{l})$	0.016
$\text{CO}_2(\text{g}) + 5\text{H}_2\text{O}(\text{l}) + 6\text{e}^- = \text{CH}_3\text{OH}(\text{l}) + 6\text{OH}^-$	-0.812
$\text{CO}_2(\text{g}) + 8\text{H}^+ + 8\text{e}^- = \text{CH}_4(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	0.169
$\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l}) + 8\text{e}^- = \text{CH}_4(\text{g}) + 8\text{OH}^-$	-0.659
$2\text{CO}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{C}_2\text{O}_4(\text{aq})$	-0.500
$2\text{CO}_2(\text{g}) + 2\text{e}^- = \text{C}_2\text{O}_4^{2-}(\text{aq})$	-0.590
$2\text{CO}_2(\text{g}) + 12\text{H}^+ + 12\text{e}^- = \text{CH}_2\text{CH}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l})$	0.064
$2\text{CO}_2(\text{g}) + 8\text{H}_2\text{O}(\text{l}) + 12\text{e}^- = \text{CH}_2\text{CH}_2(\text{g}) + 12\text{OH}^-$	-0.764
$2\text{CO}_2(\text{g}) + 12\text{H}^+ + 12\text{e}^- = \text{CH}_3\text{CH}_2\text{OH}(\text{l}) + 3\text{H}_2\text{O}(\text{l})$	0.084
$2\text{CO}_2(\text{g}) + 9\text{H}_2\text{O}(\text{l}) + 12\text{e}^- = \text{CH}_3\text{CH}_2\text{OH}(\text{l}) + 12\text{OH}^-$	-0.744

Table 1.1: Selected standards potentials in aqueous solution at 1.0 atm and 25 °C [4].

1.2 Homogeneous catalysts for CO₂ electrochemical reduction

Many compounds have been studied as homogeneous catalysts for carbon dioxide electro-reduction. In homogeneous conditions, the catalyst is considered as a shuttle between CO₂ and the electrode and the electron transferred in solution substitutes the direct electron travelling from the electrode and the substrate, as schematically shown in Figure 1.8. Reduction process is carried out at catalyst potential.

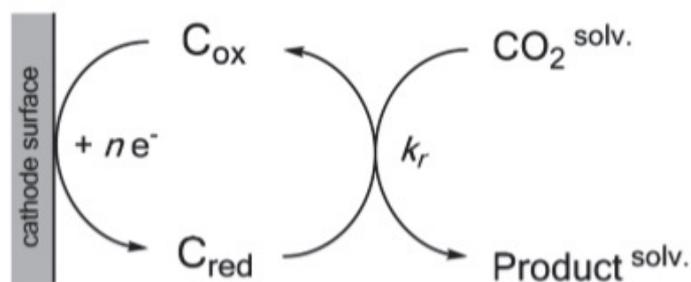


Figure 1.8: Electrochemical CO_2 reduction via homogeneous catalysis [9].

For homogeneous indirect electron transfer, two different processes can be distinguished: outer-sphere electron transfer and inner-sphere electron transfer, whose reaction steps are reported in Figure 1.9. In the first mechanism, a non-bonded electron transfer (outer-sphere) happens between CO_2 and the reduced catalyst formed (C_{red}), which acts as an outer-sphere electron mediator transporting electrons from the electrode to the substrate. The catalytic effect is visible by two phenomena; firstly, the electrons availability is increased because of the distribution over the same three dimensional spaces as the substrate (instead of a two-dimensional dispersion on the electrode surface); secondly, if fast chemical steps occur under favorable thermodynamic conditions, the equilibrium of the electron transfer is promoted in the desired direction. Protonation and radical coupling, due to the presence of CO_2 radical anion, represent rapid and thermodynamically favorable follow up reactions. The second scenario is the inner-sphere electron transfer and is equivalent to chemical catalysis; in fact, a binding interaction (chemical activation) between C_{red} and the substrate leads to the formation of a transient adduct product. Successively, thanks to follow up reaction, the catalyst is re-oxidized and the product is formed [10].

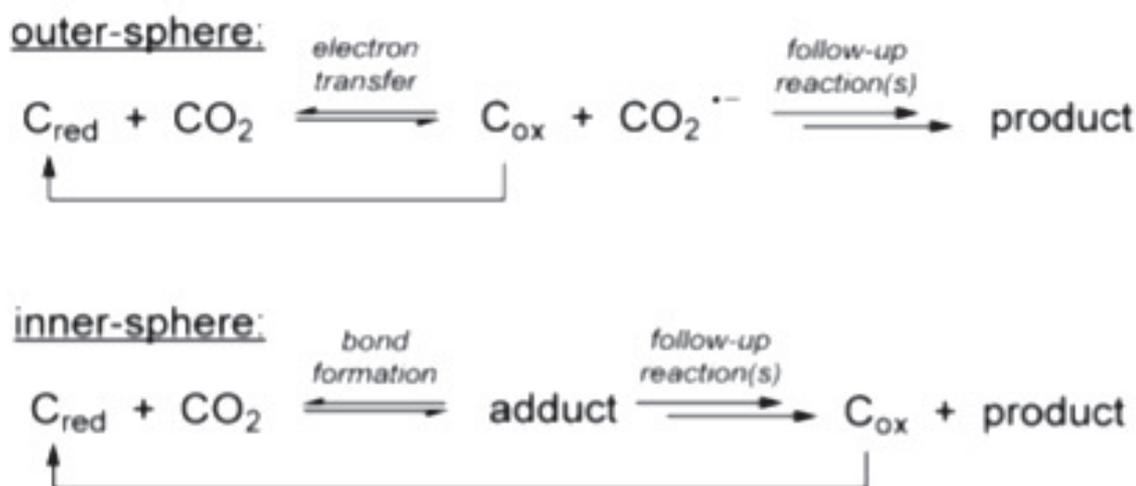


Figure 1.9: Outer-Sphere and Inner-Sphere electron transfer between a homogeneous catalyst and CO_2 [9].

Chemical catalysis represents the superior choice regarding CO_2 electro-reduction for two reasons. First, CO_2 radical anion generation is an unfavorable step associated with a high reorganization energy, in an outer-sphere electron transfer. Second, typical outer-sphere

reagents such as radical anions of hydrocarbons with extended π -systems undergo carboxylation via electrophilic aromatic substitution instead of outer-sphere electron transfer. Therefore, carbon dioxide molecule is, in most cases, activated by a chemical activation. Typically, transition metal complexes are used as CO_2 electro-reduction catalysts where metal atom is the active site. Generally, the catalyst has its reduction potential in an appropriate range; the catalyst reduced form is sufficiently stable and the chemical step is feasible under desired electrolysis conditions. An homogeneous electro-catalyst should operate close to the thermodynamic potential of the reaction, while the kinetics of the chemical step has to be fast in order to facilitate a rapid turnover. In the case of metal–organic compounds, these features can be optimized choosing a suitable metal and modifying ligand structure [10].

1.3 Heterogeneous catalysts for CO_2 electrochemical reduction

Many materials are able to interact with CO_2 or catalyst molecules before electron transfer, decreasing activation barriers and influencing reaction selectivity. They can be used to promote CO_2 electro-reduction in heterogeneous conditions and two several pathways can be followed. In the first alternative, the selected electrode itself performs as electro-catalyst and the process involves four major steps: adsorption of CO_2 molecules onto the surface of the electro-catalysts, electron transfer process, rearrangement and desorption of products (Figure 1.10) [11].

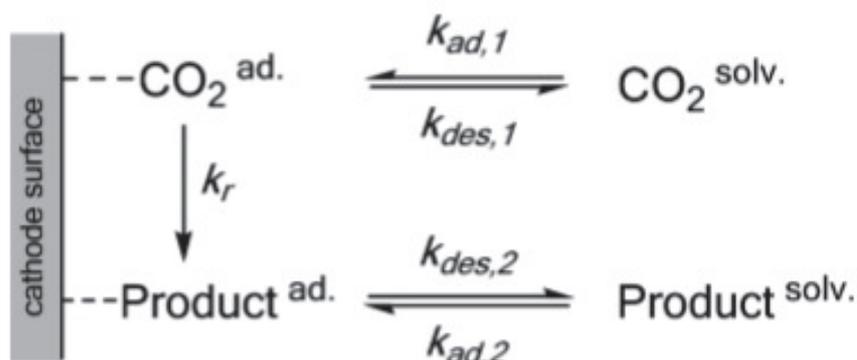


Figure 1.10: Electrochemical CO_2 reduction via heterogeneous catalysis [9].

In this context, Pt, Ag, Cu, Zn, Pd and transition metal oxides (TiO_2 , FeO_x , Cu_2O , ZnS , MoS_2) have been proved to be robust and efficient as electro-catalysts for carbon dioxide electro-reduction [11]. The choice of the electrode material is one of the factors determining the products distribution. However, the selectivity of electrode materials is difficult to predict, since the outcome depends on a number of additional parameters as type of solvent, additives, temperature, nature of supporting electrolyte, defects on the surface, etc [10].

The second alternative may consist of functionalizing and modifying the surface of the electrode. Organic metal complexes can be immobilized on the electrode surface by a multitude of approaches, forming covalent or non-covalent bonds. One method is self-assembled monolayers (SAMs), which is a simple method of modification and highly reproducible, but limited by the type of the substrate. Grafting of aryl-diazonium compounds is another interesting approach to form stable monolayers on different conductive surfaces, resulting more versatile than SAMs. The use of carbon nanotubes (CNTs) is a novel alternative for electrode

functionalization which has been investigated in the last decades. Thanks to their high surface area and good conductivity, a large amount of electrocatalytically active species can be immobilized on the electrode surface, maintaining intact electron transfer properties [12].

1.4 Homogeneous vs. heterogeneous catalysis

At the present stage, it is not simple to establish which strategy, homogeneous or heterogeneous catalysis, is more favorable for carbon dioxide electro-reduction, having both of them their advantages and drawbacks. For example, products separation and stream recycle is easier when using heterogeneous conditions rather than in homogeneous. In fact, the non-recyclable character of homogeneous catalysts impeded their application in industrial utilization, even though their excellent activity and selectivity. On the other side, in heterogeneous systems it is difficult to obtain a high selectivity due to different types of active sites. Moreover, heterogeneous catalysts present diffusion problems because it is a mass-transfer controlled reaction. A common negative aspect for both fields is the degradation of the catalyst. For homogeneous catalysis, undesired reactions could cause a slow decomposition of the molecular catalyst, while in heterogeneous case catalyst lifetime could be limited by electrode poisoning due to impurities, by-products or intermediates [10].

1.5 Elements and compounds used as catalysts for CO formation from CO₂ reduction

Carbon monoxide is one of the important molecules to use in industrial and domestic fields. To selectively produce CO, the catalysts should satisfy two requirements: a weak coordinating with CO molecules and a strong binding with the reaction intermediate [11]. Compounds that have been investigated for CO production include two groups: iron (Fe)/cobalt (Co) porphyrins and polypyridine metal complexes based on different metals such as rhenium (Re), manganese (Mn), ruthenium (Ru) and cobalt [13].

Fe porphyrin complexes are the most studied systems. Takahashi et al. have demonstrated the electro-catalytic activity for CO₂ reduction for three Fe- porphyrin complexes, producing CO with a Faradaic yield of over 94% in dimethylformaldehyde (DMF) solution. Moreover, their catalytic activity and lifetime were both increased without significant hydrogen production.[4] About this class of catalysts, the progress made in terms of ligand optimization is definitely remarkable. As a matter of fact, in a recent study, Costentin et al. found a ligand modification which could considerably speed up the rate of CO₂ electro-reduction to CO [14]. Using CNTs on glassy carbon electrode (GCE) to immobilize Fe porphyrin, catalytic activity was improved because of the direct electron transfer between Fe-porphyrin and CNTs [4]. Regarding cobalt complexes, there is a small number of examples known compared to iron porphyrins, where Co complexes represent an efficient catalyst for carbon dioxide conversion [4].

Concerning polypyridine metal complexes, they have the ability to accumulate electrons on the entire molecule and not only on the metal center, facilitating the CO₂ reduction [13]. For instance, Co terpyridine is selective for CO and H₂ production in DMF solution. For this catalyst, Fontecave et al. have reported one of the very rare examples of glassy carbon electrode functionalized by diazonium electro-grafting with a non-noble catalyst [15]. The family of manganese (Mn) and rhenium (Re) catalysts for CO₂-to-CO conversion has been frequently studied and is characterized by complexes of the type *fac*-[M(bpy)(CO)₃X] (with X= Br, Cl). Even if Mn is several orders of magnitude more abundant in the Earth's crust than Re, only recently catalytic studies have been reported about [Mn(bpy)(CO)₃Br], both in homogeneous

and heterogeneous catalysis [10]. Reinsler's group has reported the immobilization of $[\text{MnBr}(2,2'\text{-bipyridine})(\text{CO})_3]$ anchored to a carbon nanotube electrode via pyrene unit. As schematically showed in Figure 1.11, CO is the main product when high catalyst loading occurs, while formate was dominant with a lower catalyst loading [16].

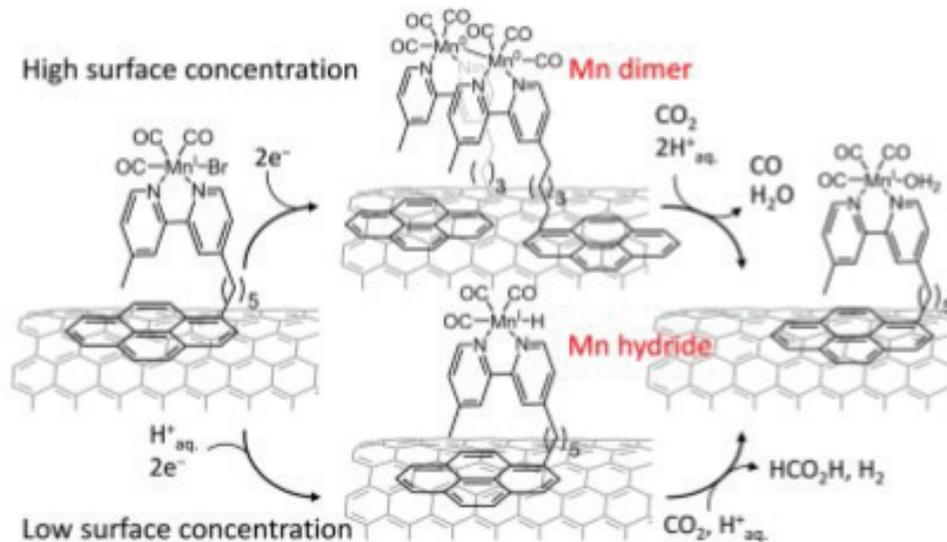


Figure 1.11: Schematic representation of $[\text{MnBr}(\text{bpy})\text{pyr}](\text{CO})_3$ immobilized on CNTs [15].

On the other hand, the first investigation about Re bipyridyl catalysts started in the early 1980s with reports of $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$ by Lehn et al. [17] and Meyer et al. [18]. The main difference to the analogous Mn catalyst is that CO_2 reduction can happen in the absence of acids, following the reductive disproportionation way: $2\text{CO}_2 + 2e^- \rightarrow \text{CO} + \text{CO}_3^{2-}$. Therefore, for Re catalyst, the carbon dioxide binding is thermodynamically preferred, while the Mn-based catalysts need a subsequent protonation as driving force [10]. About Lehn's catalyst studied in heterogeneous phase, Blackmore et al. have reported an example appending a pyrene unit to bipyridine ligand. The pyrene group served as the linker between each complex and graphitic carbon electrode surface, modified by carbon nanotubes [19]. Successively, the rhenium system was optimized via modifications of the bpy (2,2'-bipyridine) ligand with $[\text{Re}(\text{bpy}-\text{tBu})(\text{Cl})(\text{CO})_3]$, being this last the most efficient catalyst. This positive effect is due to the complexity of the bpy ligand with moieties that can optimize the electronic and steric effect of the metal complex [20]. Another class of Re-based catalysts has recently been investigated by Fontecave et al.; it is characterized by $[\text{Re}(\text{pyta})(\text{X})(\text{CO})_3]$ and $[\text{Re}(\text{tapy})(\text{X})(\text{CO})_3]$ (with $\text{X} = \text{Br}, \text{Cl}$). Figure 1.12 reports the structure of bpy, pyta (4-(2-pyridyl)-1, 2, 3-triazole derivatives) and tapy (1-(2-pyridyl)-1, 2, 3-triazole derivatives) ligand.

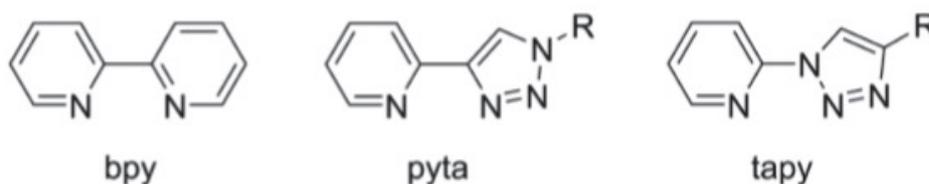


Figure 1.12: Structure of the ligand of Rhenium complexes [12].

Regarding this new series of Re pyta and Re tapy tricarbonyl complexes, the influences of the two isomeric pyridyl-triazolyl ligands and the functionalization of the pyridyl and triazolyl rings on their catalytic activity have been investigated [13]. Moreover, these functionalized ligands could be used to obtain solid electrode decorated with molecular complexes through a variety of methods by grafting them at the surface of conductive materials, such as glassy carbon. It is a non-graphitized carbon in which glassy and ceramic properties are combined with those of graphite. Because of its gas and liquid impermeability, high temperature resistance, low density and good resistance to chemical attacks, the glassy carbon material can be used as substrate for molecules immobilization and functionalized for heterogeneous CO₂ electro-reduction [21].

2. Experimental section

2.1 Materials

2.1.1 Chemicals

Anydrous solvents, including acetonitrile (ACN), dichloromethane (DCM), dimethylformamide (DMF), trifluoroethanol (TFE) and toluene were purchased by Sigma-Aldrich and used as received without further purification. Ammonium hexafluorophosphate (TBAPF₆), potassium ferrocyanide, potassium chloride, N-methylpyrrolidone and tert-butyl nitrite (tBuNO₂) were received from Sigma-Aldrich and used without extra purification. Single-walled carbon nanotube (CNT) and single-walled carbon nanotube amide functionalized were purchased by Nano-labs company.

2.1.2 Preparation and classification of Rhenium/pyta complexes.

Figure 2.1 reports the pathways followed for the [Re(pyta)(Cl)(CO)₃] synthesis, in which pyta designates 4-(2-pyridyl)-1,2,3-triazole derivatives.

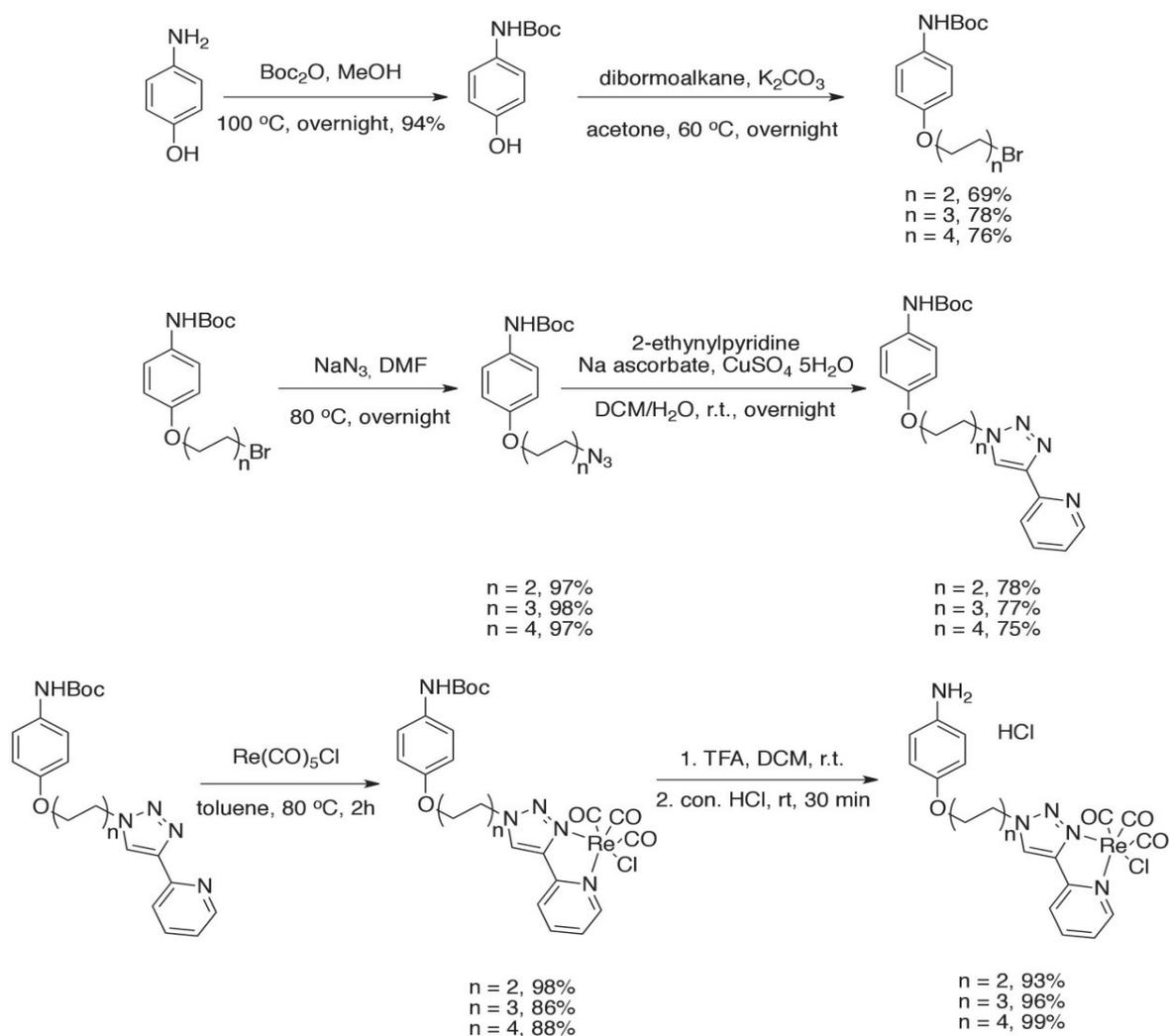


Figure 2.1: Synthesis of rhenium/pyta complexes.

The main difference between each studied rhenium complex is the side chain and depending on it, they have been categorized in four classes. An immobilization method is associated to each family. Table 2.1 reports the C1, C2, C3 and C4 complexes tested for diazonium electro-grafting and oxidative grafting. In Table 2.2 the structure of Re/pyta-COOH complex is represented and it has been used for carbon nanotubes immobilization by a peptide coupling. Table 2.3 shows the C5, C6, C7 and C8 structures to immobilize by a combination of click chemistry and diazonium electro-grafting. In the end, in Table 2.4 the Re/pyta- pyrene complexes structures that have been studied for carbon nanotubes immobilization.

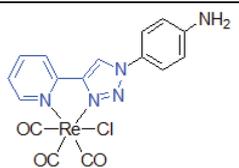
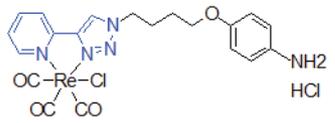
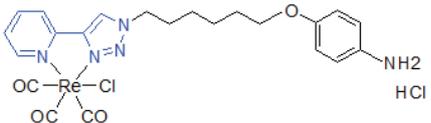
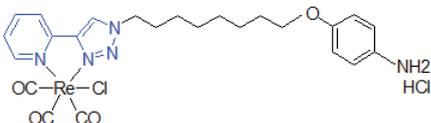
	Structure
C1	
C2	
C3	
C4	

Table 2.1: Re/pyta- aniline complexes for diazonium electro-grafting and oxidative grafting.

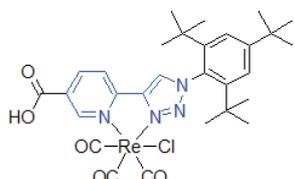
	Structure
-COOH	

Table 2.2: Re/pyta-COOH complex for carbon nanotubes immobilization by peptide coupling.

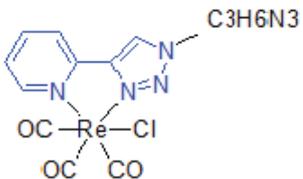
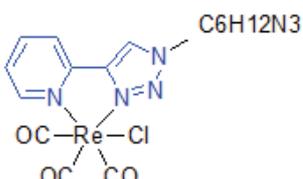
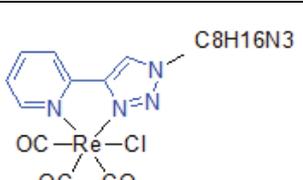
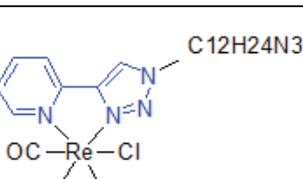
	Structure
C5	
C6	
C7	
C8	

Table 2.3: Re/pyta-N₃ complexes for click chemistry

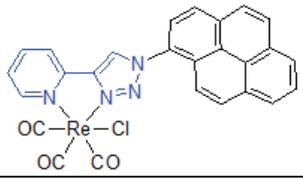
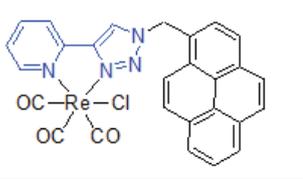
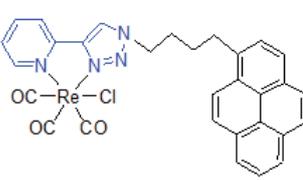
	Structure
VC-105	
VC-108	
Py/3-33	

Table 2.4: Re/pyta- pyrene complexes for immobilization on carbon nanotubes.

2.2 Methods

2.2.1 Electrochemical techniques

Electrochemical techniques are used to test and verify the catalytic activity of a complex. They were performed using a VSP Potentiostat (Bio- Logic, France). In particular, three electrochemical methods have been used in this study: cyclic voltammetry (CV), controlled potential electrolysis (CPE) and chronoamperometry (CA).

2.2.1.1 Cyclic voltammetry

Cyclic voltammetry (CV) is the main electro-analytical method used to characterize an electro-catalyst. It can be utilized to study the redox behavior in the absence of the substrate. In particular CV determines if a catalyst can be reduced within the appropriate potential regime and at which potential the electro-catalytic reaction of interest can proceed. Comparing the current peak at the potential of the catalyst, in the presence and absence of substrate, the efficiency of a catalytic process can be evaluated [10]. CV consists of linearly changing the working electrode potential from an initial value to a final value with a constant scan rate. Physically, redox reactions occur on the electrode surface and according to IUPAC convention, reduction processes correspond to negative potentials, conversely for oxidation reactions. Charge's transfer could happen through two different processes. The first one is a Faradaic process following the Faraday's law. In this case, the charge passes through electrode/electrolyte interface, as a result of an electrochemical reaction. The second one is a non-Faradaic process, which consists of an adsorption/desorption at the electrode/electrolyte surface to transfer the charge. The graph obtained from CV analysis is called cyclic voltammogram and allow to identify oxidation reaction, (positive potentials), and reduction reaction (negative potentials). Several quantitative parameters are showed on a voltammogram in Figure 2.2 such as: cathodic (E_{pc}), and anodic potential peaks (E_{pa}) cathodic (i_{pc}) and anodic current peaks (i_{pa}); cathodic half-peak potential ($E_{p/2}$) and half-wave potential ($E_{1/2}$) values [22].

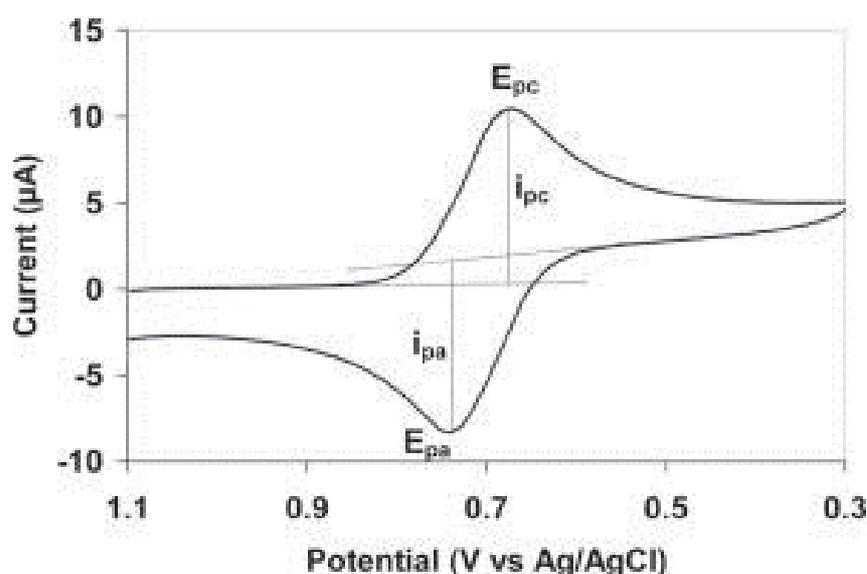


Figure 2.2: Cyclic voltammogram [31].

Remaining in the context of CO₂ electro-reduction, a typical voltammograms is reported in Figure 2.3, where the curve 1 represents the catalyst voltammetry under argon (Ar) atmosphere and the curve 2 under CO₂ atmosphere [10].

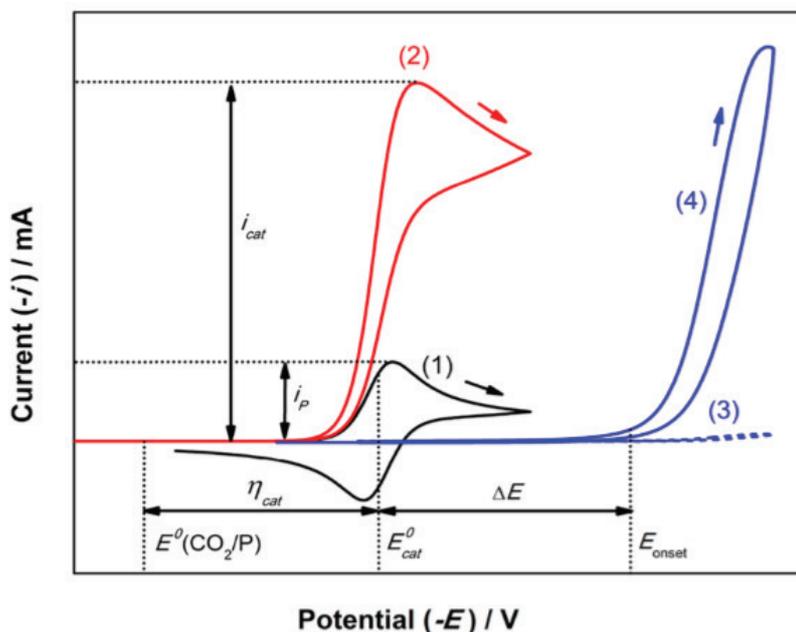


Figure 2.3: Schematic illustration of the voltammetric analysis of the electro-catalytic CO₂ reduction.

(1) CV of the catalyst under Ar. (2) CV of the catalyst under CO₂. (3)

Blank electrolyte under Ar. (4) Blank electrolyte under CO₂ [9].

Firstly, voltammetry experiments should be performed under Ar in order to know the reduction potential of the catalyst (E_{cat}^0) and its cathodic current peak. Observing the curve 1 of Figure 2.3, the feature is reversible, because the catalyst is quickly and rapidly reduced. An electrochemical process is reversible when:

$$\Delta E_P = E_{PA} - E_{PC} = \frac{59}{n} mV \quad (1)$$

(for a n electron transfer reaction) and the diffusion coefficients for the oxidized and reduced forms are the same [23], obtained from Nernst equation. When the catalyst potential has been evaluated by CV analysis under Ar, the solution can be saturated with CO₂ to repeat the experiment. As shown in curve 2 of the Figure 2.3, a catalytic current (i_{cat}) is observed under carbon dioxide atmosphere and the reversible shape of CV changes to irreversible form ($\Delta E_P > \frac{59}{n} mV$) [23]. The peaked shape depends on competition between CO₂ consumption by the rate-determining catalytic step and diffusion of fresh substrate to the electrode.

In our study, CV was carried out in a classical three electrodes single compartment cell at room temperature, using a glassy carbon working electrode (internal diameter 3 mm), a platinum wire counter electrode and a saturated Ag/AgCl reference electrode separated from the solution by a salt bridge (Figure 2.4). A volume of 10 mL of acetonitrile (ACN) solution containing 0.1 M ammonium hexafluorophosphate, as supporting electrolyte, (TBAPF₆, MW 387.43 g mol⁻¹; 1.93 g for 50 mL of solvent) was saturated with Ar or CO₂ for 15 minutes before starting CV experiment.

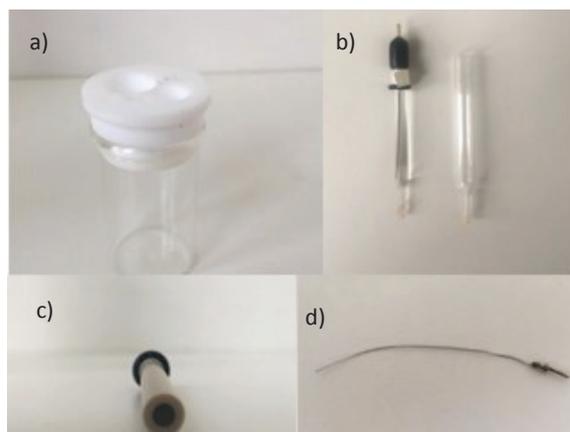


Figure 2.4: Set-up for cyclic voltammetry: a) electrochemical cell, b) reference electrode (Ag/AgCl) and salt bridge, c) working electrode (glassy carbon electrode), d) counter electrode (platinum wire).

2.2.1.2 Controlled potential electrolysis

Controlled Potential Electrolysis (CPE) is another electrochemical method which consists into fix a potential value (catalyst reduction potential) and to evaluate how the current changes over time. The potential of working the electrode is maintained constant. Usually, CPE is performed using a working electrode with a large surface area, in order to limit the duration of the measurements and also to increase current values and product formation. The solution is continuously stirred during the experiment to maintain a thin diffusion layer [24]. CPE were carried out in two electrochemical compartment cell (Figure 2.5). The cathodic compartment included a glassy carbon plate as working electrode (internal diameter equal to 15 mm, Figure 2.5a), was separated from the anodic compartment via a fine porous frit. The reference electrode was a saturated Ag/AgCl electrode and was separated from the solution by a salt bridge. A platinum wire, used as counter electrode, was in the anodic compartment. An acetonitrile solution at 0.1 M of TBAPF₆ in the cathodic side and one at 0.4 M in the anodic side were saturated with CO₂ for one hour before starting the CPE. The cathode compartment volume was 7.5 mL and the anode compartment volume 4 mL. CPE was performed for 2 hours. Usually, before using the electrochemical cell, it was left overnight in H₂PO₄/ H₂O₂ acid to be cleaned, was sonicated with water for 1 hour and dried in the oven for 30 minutes.

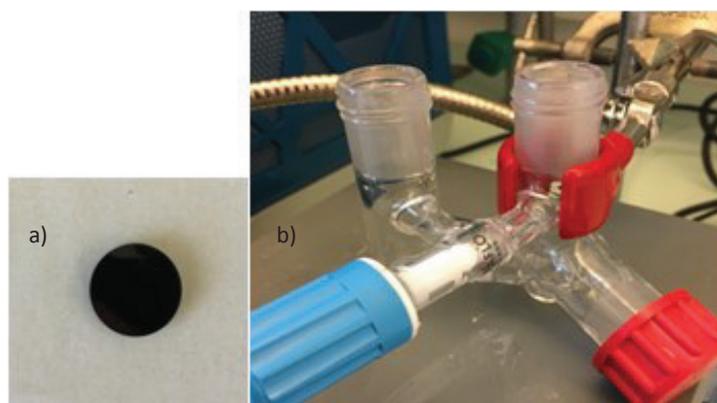


Figure 2.5: Set- up for controlled electrolysis potential: a) working electrode (glassy carbon plate), b) electrochemical cell with three ways.

2.2.1.3 Chronoamperometry

Chronoamperometry (CA) is an electrochemical pulsed technique in which a potential step is applied to the working electrode and the resulting current from faradaic processes is monitored as function of the time. It is used to examine diffusion processes, adsorption and the kinetics of chemical reactions [25]. The CA produces high charging currents, which decay exponentially with the time. Before starting the experiment, the electrode potential is maintained at a value at which faradaic process does not occur; then, it is stepped to the required value for the start of redox reactions. The Faradaic current obeys the Cottrell equation (2):

$$i(t) = \frac{nFAD^{1/2}C_0}{\pi^{1/2}t^{1/2}} \quad (2)$$

where n is the number of electrons in the redox process, F the Faraday constant, A the electrode area, D the diffusion coefficient of the redox species, C_0 is the bulk concentration of the redox species, and t is time.

2.2.1 Chemical analysis

During controlled potential electrolysis experiment, H₂ and CO production were monitored by gas chromatography, taking a gas sample of 50 μL. For H₂, measurements were performed by gas chromatography on Shimadzu GC- 2014 equipped with a Quadrex column, a thermal conductivity detector, using N₂ as a carrier gas. CO was measured using a Shimadzu GC- 2010 Plus gas chromatography , fitted with a Restek Shin Carbon column, helium carrier gas, metanizer and flame ionization detector. After CPE, a sample was analyzed using a Metrohm 883 Basic IC plus exchange chromatography instrument, Metrosep A Supp 5 column and conductivity detector. A sample of 100 μL of solution, diluted with water, was injected into the instrument to measure formate concentration.

2.2.2 Catalyst immobilization methods

2.2.2.1 Diazonium electro-grafting

Re/pyta- aniline complexes can be immobilized on the electrode surface by diazonium electro-grafting because of the presence of amine (NH₂) group. Diazonium electro-grafting is divided in two steps (Figure 2.6): the first step is a chemical step called diazotization while the second one is an electrochemical reduction.

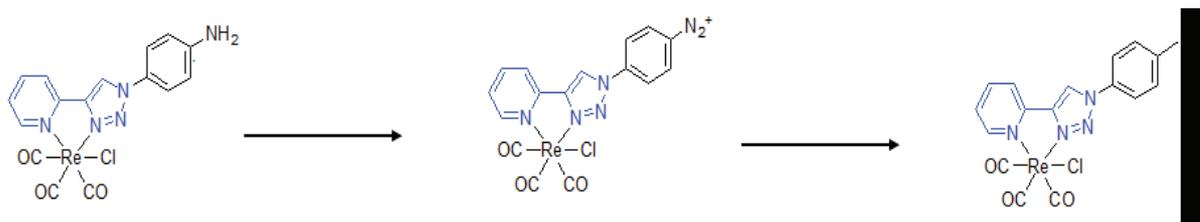


Figure 2.6: Steps of diazonium electro-grafting for Cl.

Using the set-up reported in Figure 2.4, Re/pyta- aniline complex (0.5 mM) was dissolved in 10 mL of ACN solution containing TBAPF₆ (0.1 M, MW 387.43 g mol⁻¹, 386 mg) and then 10 mM of *tert*-butyl nitrite, as reactant, (tBuNO₂, MW 103.12 g mol⁻¹, 12 μL), was added in solution. The bare polished glassy carbon electrode was immersed in the solution and the system was degassed with Ar for 10 minutes in dark conditions. A diazonium salt was obtained as reaction product and it was covalently immobilized on the electrode surface by electrochemical reduction. Electro-grafting was achieved by cycling the potential from + 0.4 V to - 0.6 V for 20 scans at 20 mV s⁻¹. After immobilization phase, the grafted electrode was washed with H₂O and ACN to remove not grafted materials and characterized by cyclic voltammetry [26]. The same procedure with a different amount of *tert*-butyl nitrite (15 μL) was followed for the set-up of Figure 2.5.

2.2.2.2 Oxidative grafting

Oxidative grafting is an electro-chemical immobilization method. Catalyst molecules can be covalently fixed on the electrode surface thanks to the one-electron oxidation of amine (NH₂) group (Figure 2.7). The radical reacts with the carbon surface stabilizing a covalent attachment of the compound via amine linkage [27].

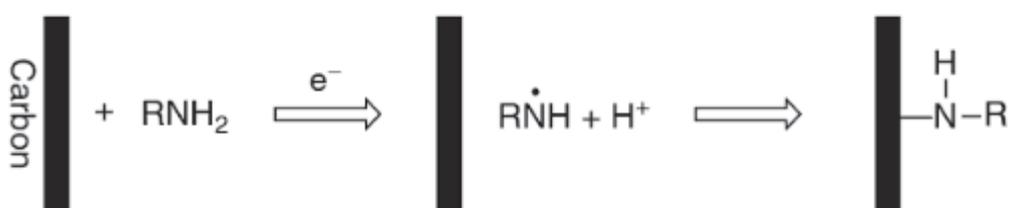


Figure 2.7: Step of oxidative grafting [27].

Oxidative grafting is typically conducted in anhydrous solvent. In fact, 0.5 mM of Re/pyta-aniline complex was dissolved in 10 mL solution of ACN containing 0.1 M of TBAPF₆. The solution was purged with Ar for 15 minutes and a chronoamperometry was done at + 1.3 V, as working electrode potential and a subsequent cyclic voltammetry was done for electrode characterization.

2.2.2.3 Immobilization on carbon nanotubes surface by peptide coupling

Carboxyl unit in Re/pyta-COOH complex allows to bond the molecule to the carbon nanotube amide functionalized surface by a peptide coupling. In Figure 2.8 a general schematic peptide coupling is represented.

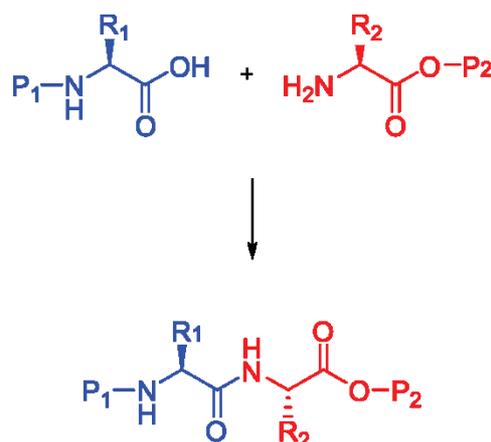


Figure 2.8: Schematic peptide coupling reaction[33].

Single-walled carbon nanotubes (SWCNTs) amide functionalized were made by Electric Arc Discharge method. with a purity more than 90 % and diameter from 4 to 6 nm and a length from 0.7 to 1 μm . A suspension of N-methyl-2-pyrrolidone and SWCNTs amide functionalized was prepared at a concentration of 5 mg mL^{-1} . The suspension was sonicated in water for 30 minutes and 2 μL of it was deposited by drop-casting onto glassy carbon electrode surface (internal diameter 3 mm). After drying process in the oven for 10 minutes, the modified electrode was soaked in acetonitrile solution containing 1 mM of catalyst for 30 minutes in dark conditions. CV was used to characterize the functionalized electrode [19].

2.2.2.4 Non-covalent immobilization on carbon nanotubes

The presence of pyrene ring in Re/pyta- pyrene complexes allows their immobilization onto carbon nanotubes (CNTs) surface. It is a non-covalent binding because of the physical interaction between pyrene unit and CNTs surface (Figure 2.9). Strong Van der Waals π - π interactions between polyaromatic hydrocarbons and graphitized carbon surface may occur [28]. The substrate was a polished glassy carbon electrode (GCE) in order to afford conducting surfaces.

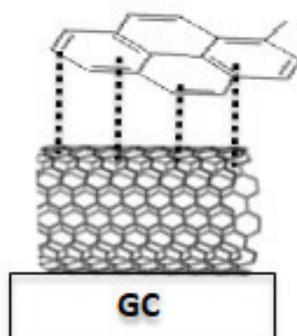


Figure 2.9: Physical adsorption of Pyrene ring on SWCNTs immobilized on GCE surface.

Single walled carbon nanotubes were synthesized by chemical vapor deposition (CVD) with purity higher than 95 %. They were purchased from Sigma- Aldric (diameter of 1.5 nm and length of 1.5 μm). This kind of immobilization consists of two steps: carbon nanotubes

immobilization on the electrode surface and physical adsorption of catalysts molecules via pyrene ring. Firstly, a suspension of CNTs and N-methyl-2-pyrrolidone (5 mg mL⁻¹) was prepared and was sonicated for 30 minutes in H₂O. Then, 2 μL of suspension was drop casted on GCE (0.3 cm diameter) surface and then, drying process occurred in the oven for 10 minutes. The modified electrode was functionalized with a catalyst by soaking for 30 minutes in dark conditions in a solution of dimethylformamide (DMF) containing 1 mM of catalyst [19]. Successively, it was rinsed with DMF and ACN to remove loosely bound complexes. CV was used to characterize the CNTs-modified electrode. The same procedure was followed for the functionalization of glassy carbon plate (15 mm of diameter) covered with a suspension drop of 15 μL.

2.2.3 Useful notations

Faradaic efficiency (FE)

FE is the percentage of electrons employed to generate a desired product. It can be calculated dividing the moles of consumed electrons during the reaction by the moles of electrons transferred from anode to cathode by Faraday Law [11].

$$FE = \frac{\alpha * n * F}{Q} \quad (3)$$

where Q is the passed charge, α is the number of transferred electrons, n the number of produced moles and F is the Faraday constant (96485 C mol⁻¹).

Calculation of surface electrode coverage

The electrode surface coverage (Γ) is calculated by the integration of the cyclic voltammogram area using Laviron equation (4):

$$\Gamma = \frac{Q}{n * F * A} \quad (4)$$

where Q is the charge, n the electrons number, A the electrode area and F the Faraday constant [29].

3. Results and discussion

In this section, the results about the rhenium/pyta complexes for the electro-reduction of CO₂ are reported. Rhenium complexes are tested by electrochemical techniques explained in the previous section. This third section is divided by the type of complex and their deposition method. We studied two different kind of deposition on the GCE surface. The first one involves a covalent bond between catalysts molecules and electrode atoms; this kind of immobilization interests Re/pyta- aniline complexes, Re/pyta- N₃ complexes and Re/pyta- COOH complex. Re/pyta- aniline complexes have been immobilized by diazonium electro-grafting and oxidative grafting. Re/pyta- N₃ complexes may be immobilized by click chemistry and Re/pyta- COOH complex with carbon nanotubes immobilization by peptide coupling. The second type of immobilization consists of stabilize a physical interaction between the catalyst and the electrode surface modified by carbon nanotubes structures. μ

3.1 Covalent immobilization

3.1.1 Re/pyta- aniline complexes for diazonium grafting

The structures of Re/pyta-aniline complexes for the electro- grafting are reported in Table 3.1. The difference from each complex is the length of the side chain. In fact, the number of carbon atoms, which bonds the ligand to the benzene ring, changes from C1 compound to C4 one.

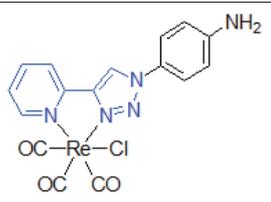
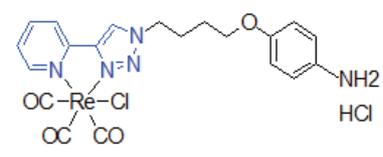
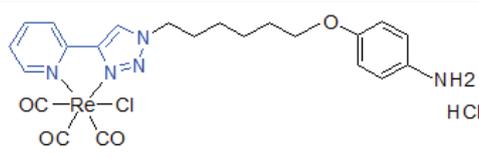
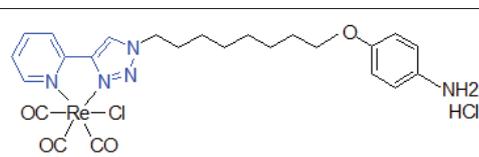
	Structure
C1	
C2	
C3	
C4	

Table 3.1: Re/pyta- aniline complexes for diazonium electro-grafting and oxidative grafting.

Firstly, the electrochemical behavior of C1, C2, C3 and C4, at a concentration of 0.5 mM, were studied by cyclic voltammetry at 100 mV s^{-1} in argon and CO_2 saturated ACN (10 mL) containing TBAPF_6 (0.1 M), as supporting electrolyte, using a glassy carbon electrode. The choice of acetonitrile as electrolyte solvent is due to the solubility of rhenium complexes and of carbon dioxide (8 times higher than in water) [30]. CVs are referenced to Ag/AgCl electrode. Figure 3.1, 3.2, 3.3 and 3.4 show CVs of C1, C2, C3 and C4 respectively. The potential window goes from -2 V to $+0.5 \text{ V}$. Observing blue curves (CVs under Ar atmosphere), a first irreversible reduction peak is visible around -1.45 V and it could be assigned to chloride reduction. Scanning toward more negative potentials, a second irreversible feature is observed for each complex. This feature has been assigned to the reduction of ligand and the reduction potential is: -1.66 V for C1, -1.6 V for C2, -1.68 V for C3 and -1.7 V for C4. It has almost the same value although the different length of the side chain. Regarding red curves (CVs under CO_2 atmosphere), the catalytic current is recorded and the most negative is assigned to C1.

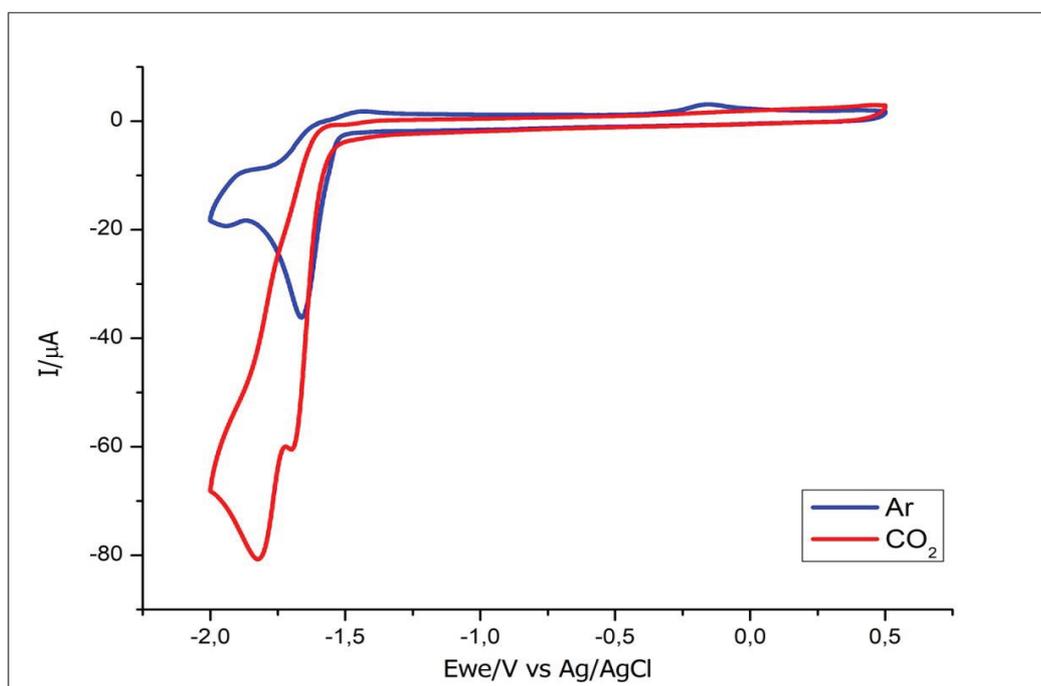


Figure 3.1: CVs of 0.5 mM of C1 in ACN with 0.1 M of TBAPF_6 under Ar (blue curve) and under CO_2 (red curve) recorded at 100 mV s^{-1} at a glassy carbon electrode.

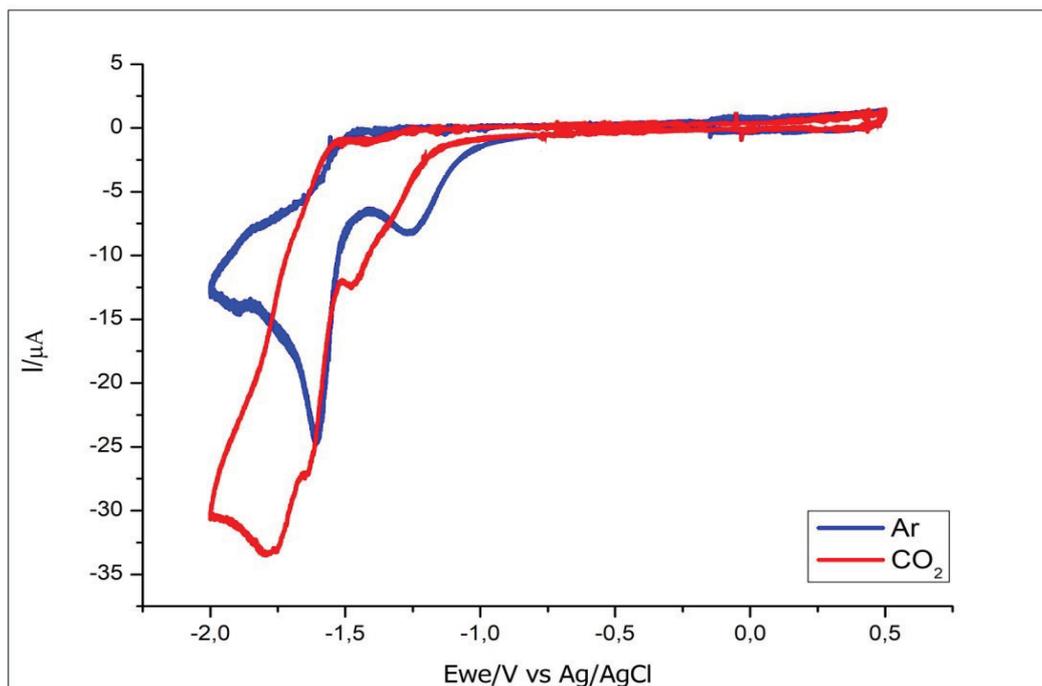


Figure 3.2: CVs of 0.5 mM of C2 in ACN with 0.1 M of TBAPF₆ under Ar (blue curve) and under CO₂ (red curve) recorded at 100 mV s⁻¹ at a glassy carbon electrode.

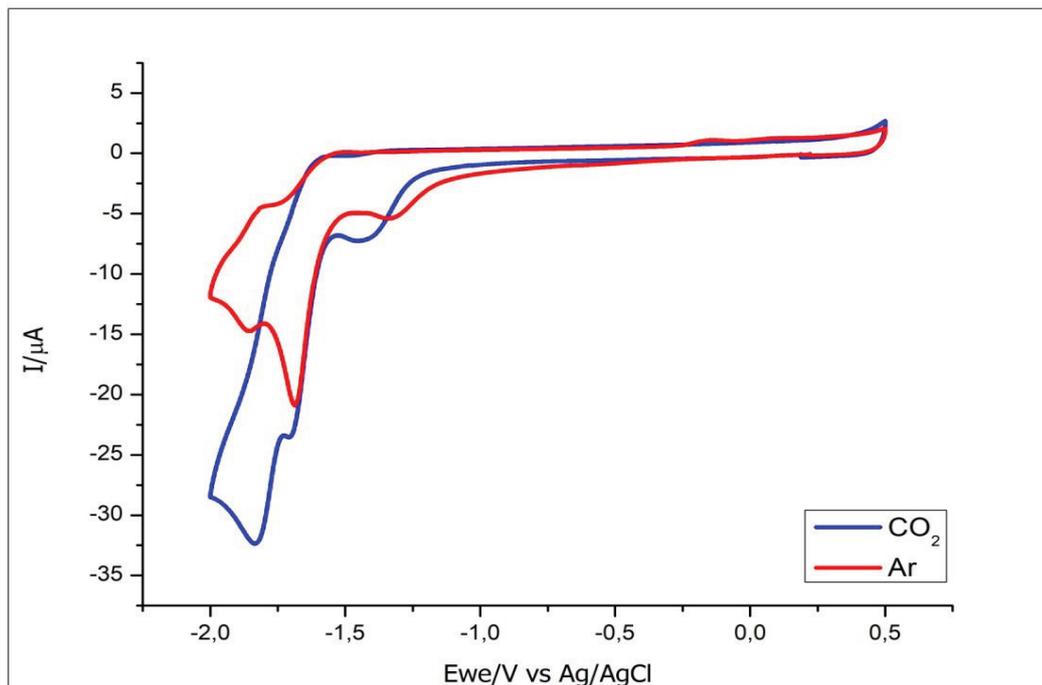


Figure 3.3: CVs of 0.5 mM of C3 in ACN with 0.1 M of TBAPF₆ under Ar (blue curve) and under CO₂ (red curve) recorded at 100 mV s⁻¹ at a glassy carbon electrode.

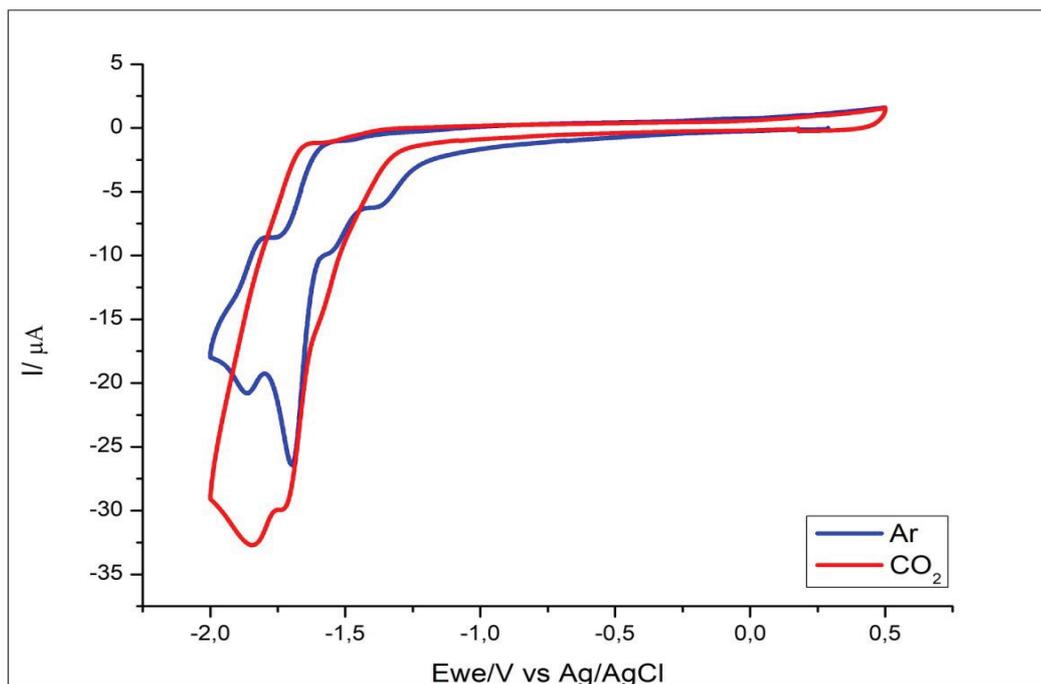


Figure 3.4: CVs of 0.5 mM of C4 in ACN with 0.1 M of TBAPF₆ under Ar (blue curve) and under CO₂ (red curve) recorded at 100 mV s⁻¹ at a glassy carbon electrode.

Figure 3.5 reports CVs of blank solution (red curve), of C1 under N₂ (blue and green curve) with a larger potential window from -2 V to +2 V. Scanning toward positive potential, a first irreversible oxidation is observed at +1.24 V vs. Ag/AgCl, associated with NH₂ oxidation. A second oxidation peak around +1.48 V is due to oxidation of couple Re^I/ Re^{II} and the last one is around +1.93 V is assigned to the oxidation of ligand.

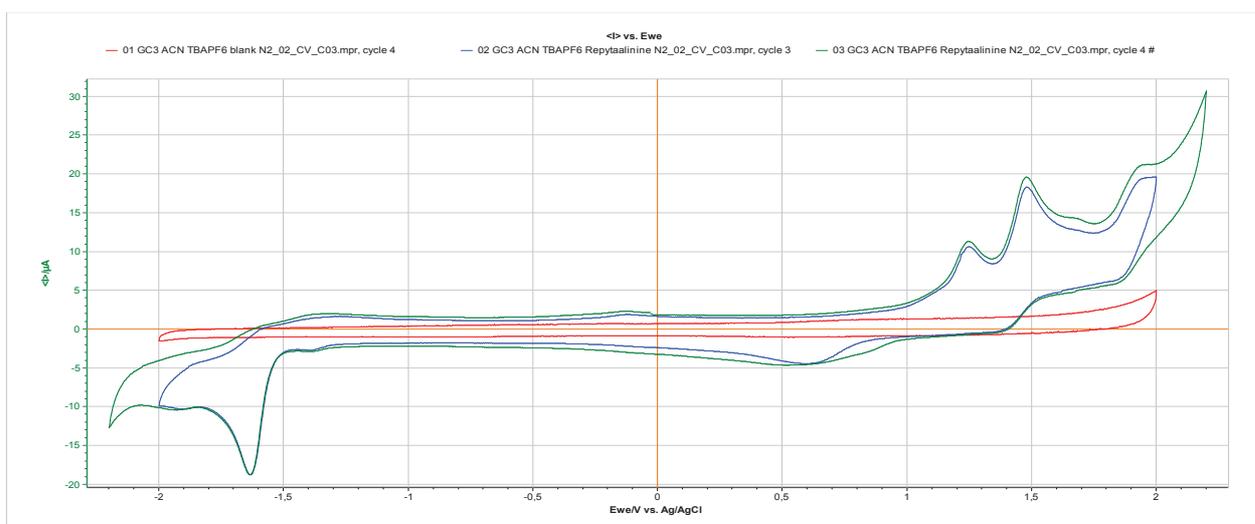


Figure 3-5: CVs of blank in ACN with 0.1 M of TBAPF₆ under N₂ (red curve), CVs of 0.5 mM of C1 in ACN with 0.1 M of TBAPF₆ under N₂ (blue and green curves) recorded at 100 mV s⁻¹ at a glassy carbon electrode.

The addition of increasing amounts of trifluoroethanol (TFE), as proton source, shows a more negative catalytic current (Figure 3.6). TFE was added in 5 %, 10 % and 20 % v/v and a good catalytic process is assigned to the lowest percentage even though the reduction potential peak is not shifted toward more positive value (- 1.7 V).

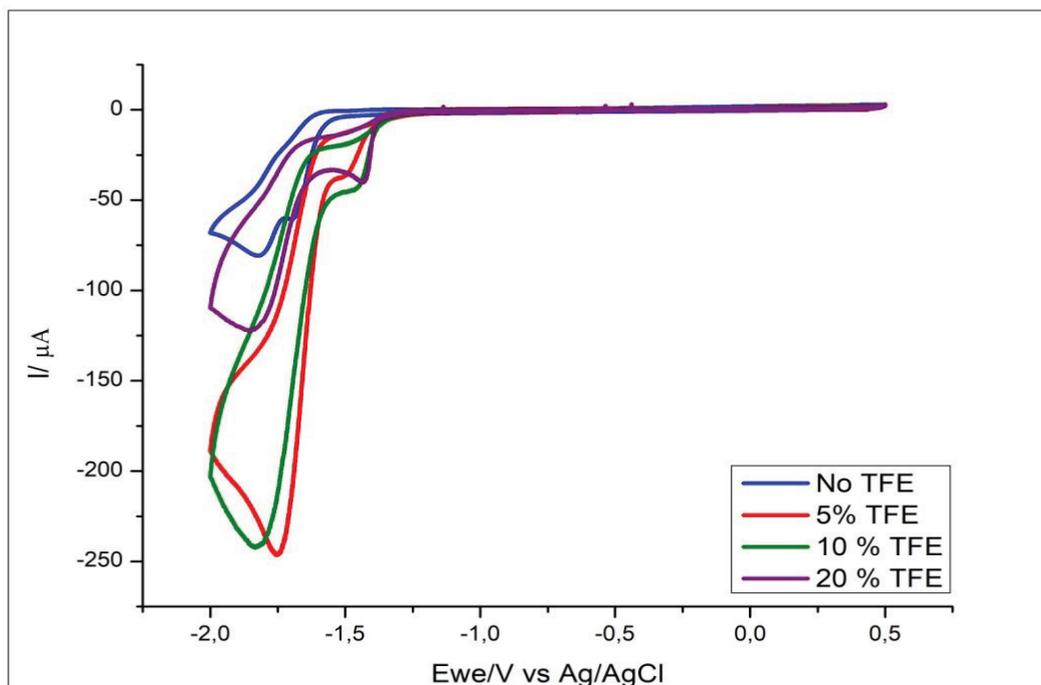


Figure 3.6: CVs of 0.5 mM of C1 in ACN with 0.1 M of TBAPF₆ under CO₂ (blue curve) adding 5 % of TFE (red curve), 10 % of TFE (green curve) and 20 % of TFE (purple curve) recorded at 100 mV s⁻¹ at glassy carbon electrode.

To study the catalytic behavior in heterogeneous phase, diazonium electrografting was performed for Re/pyta-aniline complexes, following the procedure reported in the previous section. Grafting was started by cycling the potential from + 0.4 V to - 0.6 V at 20 mV s⁻¹ for 20 scans (Figure 3.7). The only intense peak is observed at + 0.4 V and it is associated with electro-reduction of diazonium salt, produced by diazotization step. The intensity peak decreases by successive scans because of the covalent coupling of the complex to the glassy carbon surface. Figure 3.7 reports the CV of the diazonium grafting of C1, which resulted similar for all complexes (C2, C3 and C4).

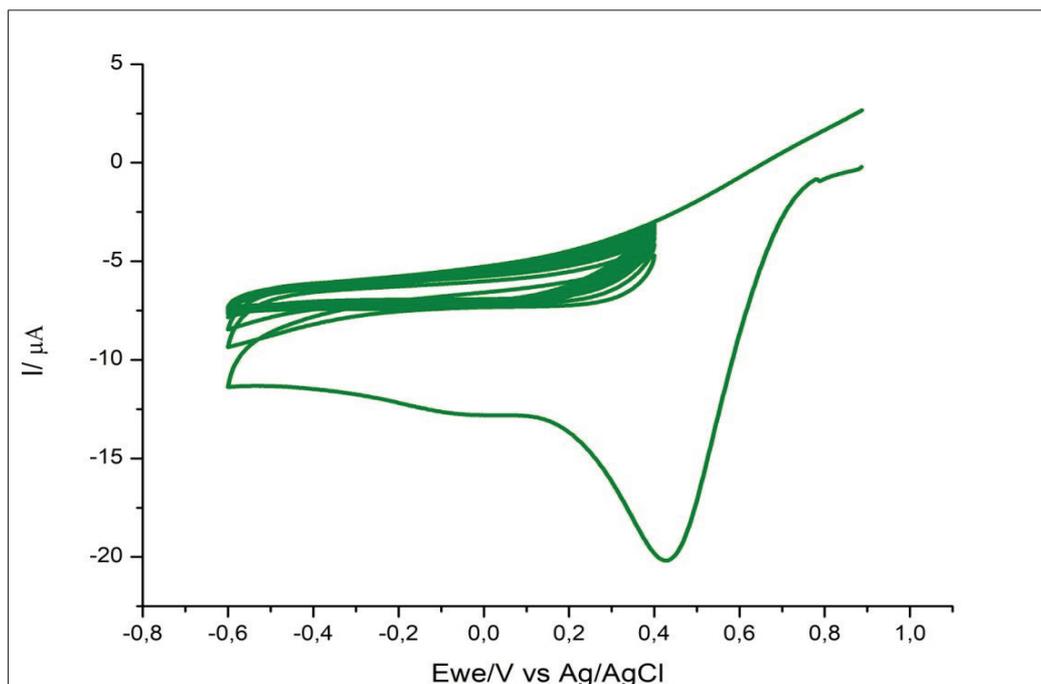


Figure 3.7: CV characterization grafted electrode (0.5 mM of Cl in ACN with TBAPF₆ purged Ar) recorded at 20 mV s⁻¹.

The grafting of the electrode was confirmed by interrogating the surface towards a redox probe (potassium ferrocyanide). A cyclic voltammetry was carried out in 1 mM of Fe(CN)₆⁴⁻ in 0.5 M KCl. The grafted electrode was washed with ACN and H₂O and a CV in Fe(CN)₆⁴⁻ was performed. In Figure 3.8, CVs in potassium ferrocyanide solution for the bare GCE (red curve) and the grafted GCE (blue curve) are compared. The potential is cycling from -1 V to +1 V at 100 mV s⁻¹ for 10 scans. The reduction and oxidation peaks observed for the red curve are assigned to the transition of reduction state from Fe^{III} to Fe^{II} and to the oxidation state. In the grafted electrode case, the electro-grafted layer on the surface does not permit the iron redox process and therefore, any peak is not visible.

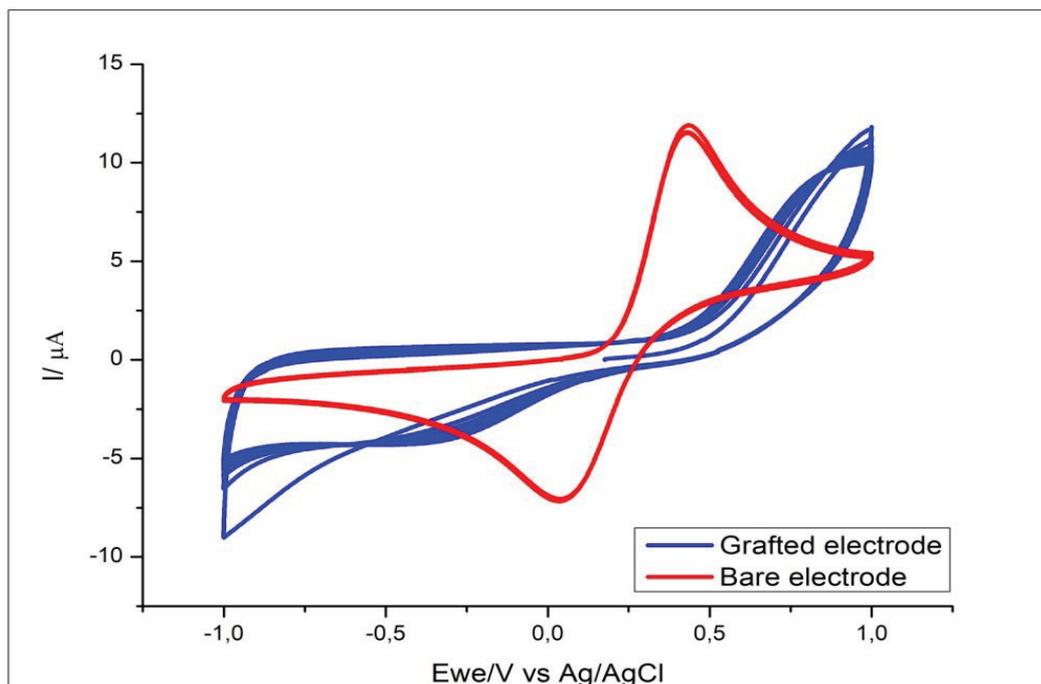


Figure 3.8: CVs of 1 mM of $\text{Fe}(\text{CN})_6^{4-}$ in 0.5 M of KCl under Ar recorded at 100 mV s^{-1} at bare (red curve) and grafted (blue curve) glassy carbon electrode.

Electrode characterization was also done by cyclic voltammetry in ACN/ 0.1 M of TBAPF_6 under Ar (Figure 3.9) and under CO_2 (Figure 3.10), cycling the potential from - 2 V to 0.5 V at 100 mV s^{-1} . Compared Figure 3.9 to homogeneous conditions (Figure 3.1), the reduction peak potential is still -1.67 V and the current is less negative. By equation (4), the amount of the molecules on the electrode surface was calculated integrating CV under Ar. The coverage order is nanomol cm^{-2} for each complex. Observing Figure 3.10, CVs after grafting under CO_2 show an onset potential (- 1.4 V) lower than the one in Figure 3.1 (-1.68 V). In the other hand, a current decrease is recorded after the first cycle and it could be assigned to the loss of the catalyst layer from the electrode surface.

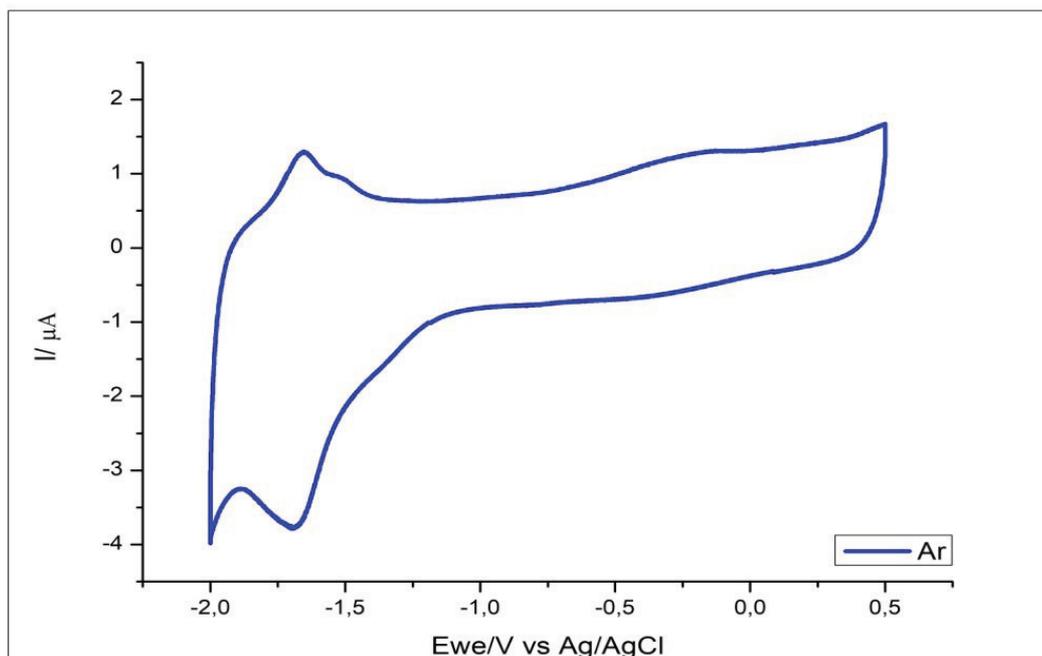


Figure 3.9: CV of C3 in ACN with 0.1 M of TBAPF₆ under Ar recorded at grafted glassy carbon electrode (3rd cycle).

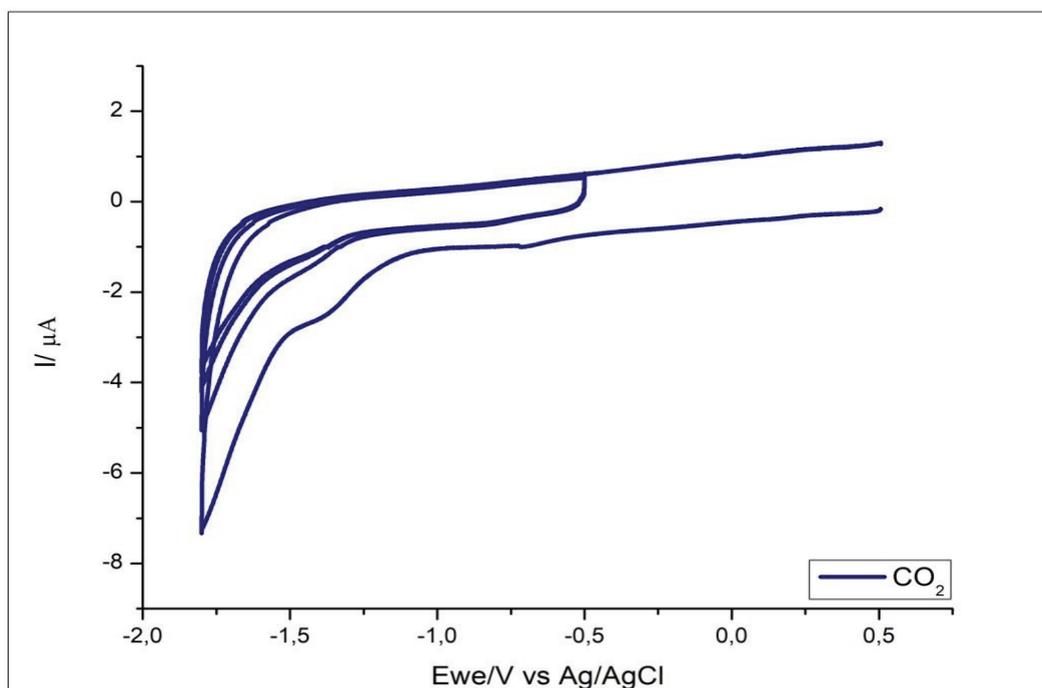


Figure 3.10: CVs of C1 in ACN with 0.1 M of TBAPF₆ under CO₂ (blue curves) recorded at 100 mV s⁻¹ at grafted glassy carbon electrode.

In addition, CVs after grafting were carried out with different scan rate values, reported in Table 3.2. The important result obtained is the linear dependence between scan rate and current, as

reported in Figure 3.11. Therefore, the system is under adsorption control and the catalyst is confined on the electrode surface. Conversely, a linear relation between the square root of the scan rate and the current would indicate that the active species are molecular in nature and they work in a diffusion- controlled regime [13].

Scan rate (mV/s)	I (μ A)
25	0,532
50	0,772
75	0,901
100	1,05
250	2,309
500	3,88
750	5,09
1000	6,04

Table 3.2: Scan rate vs. cathodic current peak values of CVs of C3 in ACN with 0.1 M of TBAPF₆ under Ar recorded at grafted glassy carbon electrode.

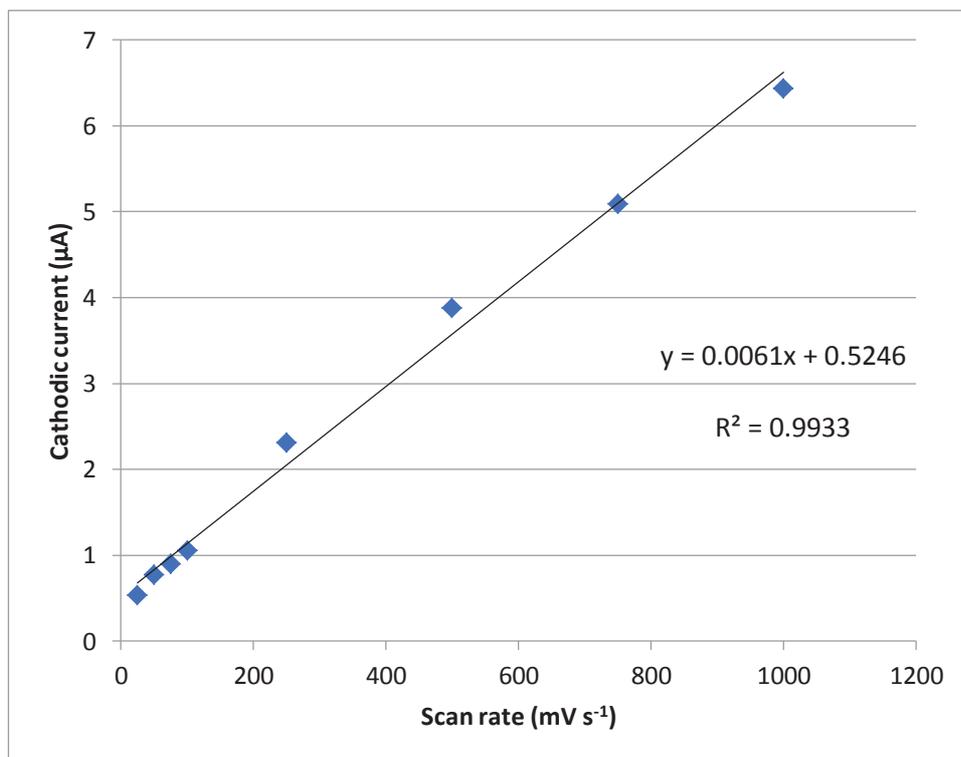


Figure 3.11: Cathodic current trend with different scan rate.

In contrast, soaking again the GCE in potassium ferrocyanide solution after cycling under Ar and CO₂, CVs, reported in Figure 3.12 (red curve), is not flat anymore, but iron reduction and oxidation peaks are observed and the catalyst layer is lost. Thus, we cannot evidence an electro-grafted layer anymore.

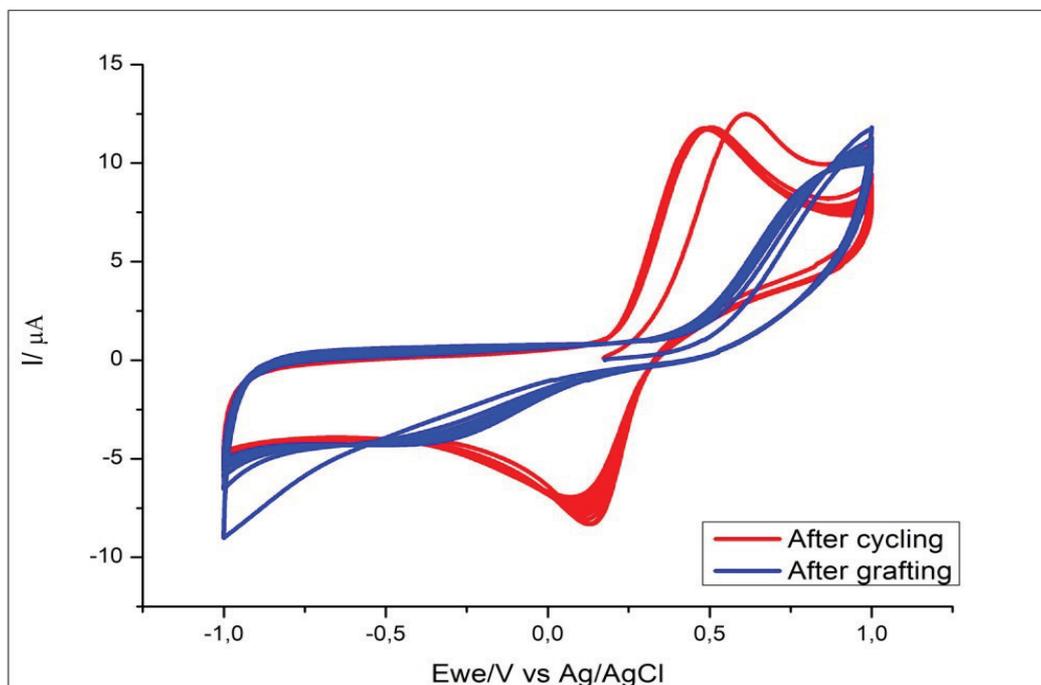


Figure 3.12: CVs of $Fe(CN)_6^{4-}$ in H_2O/KCl recorded at 100 mV s^{-1} at grafted (blue curve) and grafted after cycling (red curve) glassy carbon electrode.

To further characterize the catalyzed reaction, controlled potential electrolysis of CO₂-saturated ACN/0.1 M of TBAPF₆ solution was performed using C1, C2 and C3 grafted on the GCE electrode applying a potential of - 1.7 V (the reduction potential of Re/pyta- aniline complexes). Figure 3.13 reports current trend vs. time during 2 hours of CPE for blank solution (purple curve), C1 (blue curve), C2 (red curve) and C3 (green curve). The current intensity remains approximately constant and stable for 2 hours of the experiment. In the other hand, in Figure 3.14 charge trend vs. time is shown.

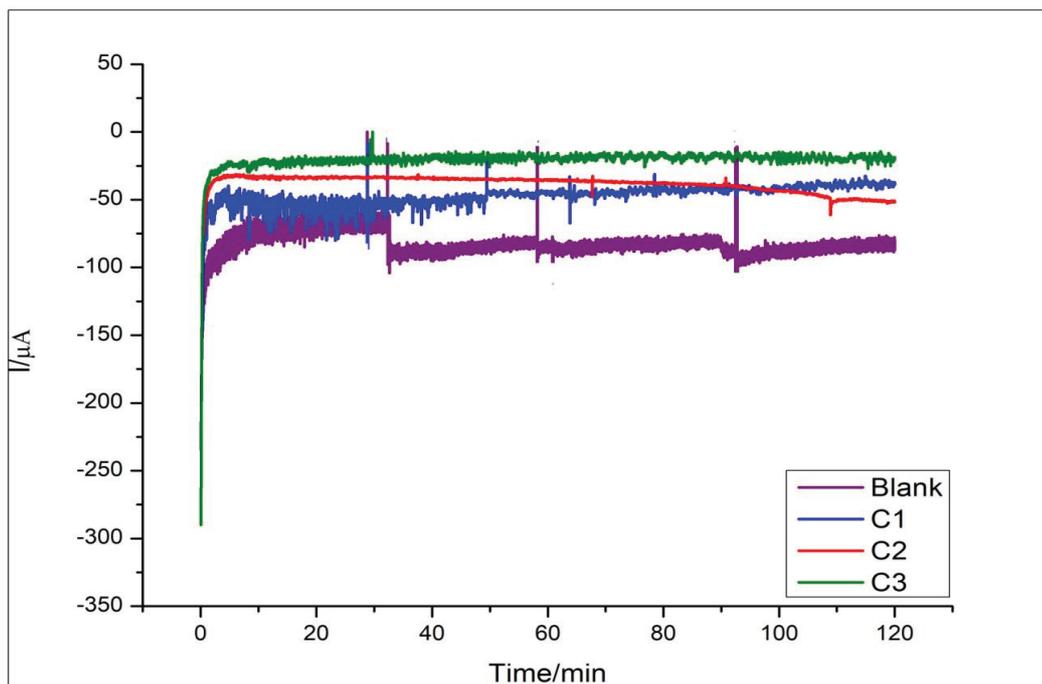


Figure 3.13: CPE (Current vs Time) in ACN with 0.1 M of TBAPF₆ purged CO₂ recorded at grafted glassy carbon electrode: blank (purple curve), C1 (blue curve), C2 (red curve), C3 (green curve).

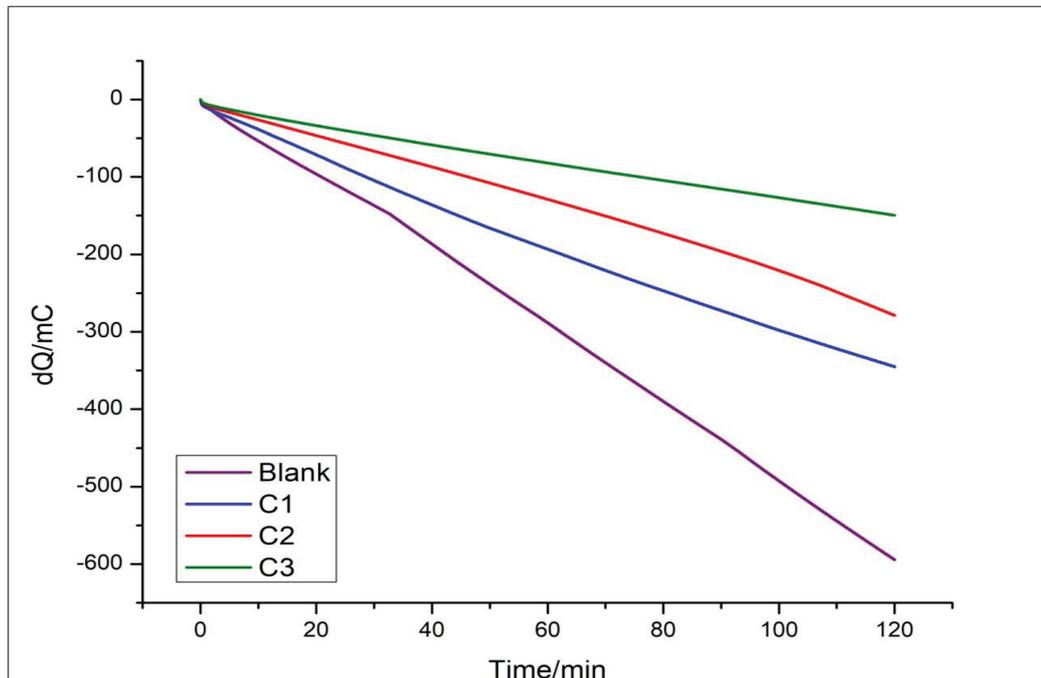


Figure 3.14: CPE (Charge vs Time) in ACN with 0.1 M of TBAPF₆ purged CO₂ recorded at grafted glassy carbon electrode: blank (purple curve), C1 (blue curve), C2 (red curve), C3 (green curve).

During CPE, CO and H₂ were detected by gas chromatographic analysis. Any formate was observed by ion-exchange chromatography. Table 3.3 reports the results obtained after 2 hours of electrolysis in terms of CO and H₂ production. C1 produces more moles of CO than C2 and C3, but a similar amount of hydrogen is measured. As it is easy to see, while C1 and C2 complexes give significant amount of H₂, C3 is much more selective for carbon monoxide production. In terms of Faradaic efficiency, it reaches a value of 46.8 % for CO and just 8 % for hydrogen production (for grafted C3).

	$\mu\text{mol CO}$	$\mu\text{mol H}_2$	dQ/C	FE CO	FE H ₂
Blank	0	0.23	0.594	4.9 %	7.7 %
C1	0.247	0.246	0.345	27.6 %	29.5%
C2	0.12	0.20	0.278	17 %	28.3 %
C3	0.18	0.03	0.15	46.8%	8%

Table 3.3: Amount of CO and H₂, charge and Faradaic efficiency after 2 hours of CPE.

Figure 3.15 reports the trend of CO moles produced by each catalyst during CPE. C1 remains the one that produces more CO than the others, but giving the same amount of hydrogen. C2 does not show a good activity after 30 minutes because its CO production remain constant. In the other hand, C3 generates an increasing amount of carbon dioxide during the CPE performance, not promoting proton reduction.

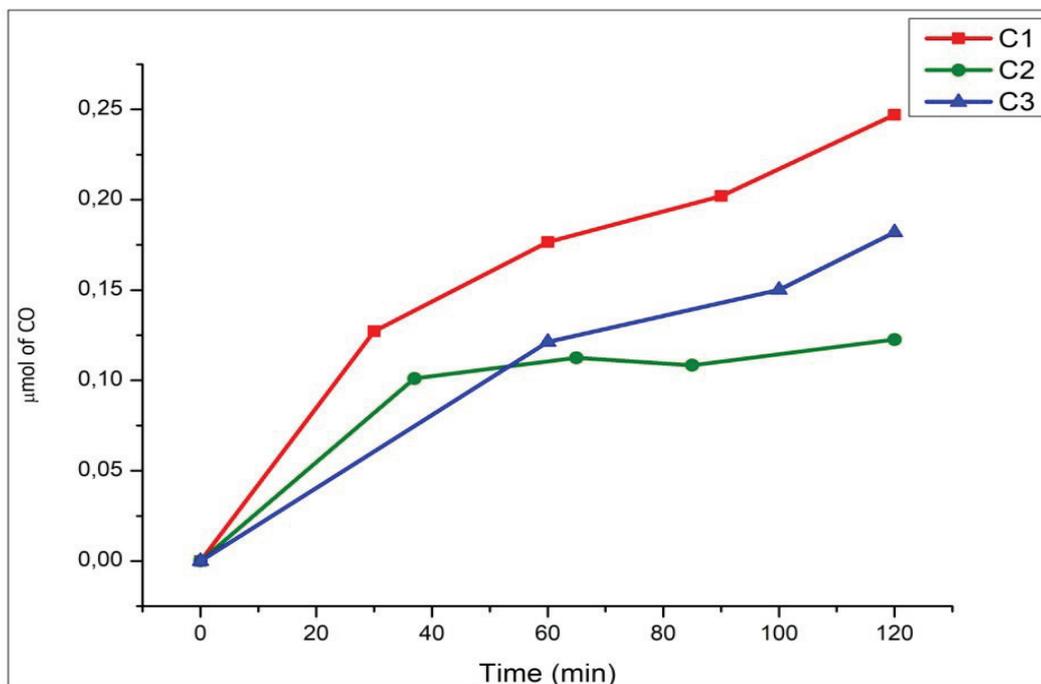


Figure 3.15: Amount of CO produced after 2 hours of CPE by C1 (red curve), C2 (green curve) and C3 (blue curve).

3.1.2 Re/pyta- aniline complexes for oxidative grafting

Re/pyta-aniline complexes were also immobilized by oxidative grafting. Figure 3.16 shows the chronoamperometry at +1.3 V for 30 minutes for C1 complex (0.5 mM) in Ar-saturated 0.1 M of TBAPF₆ in ACN.

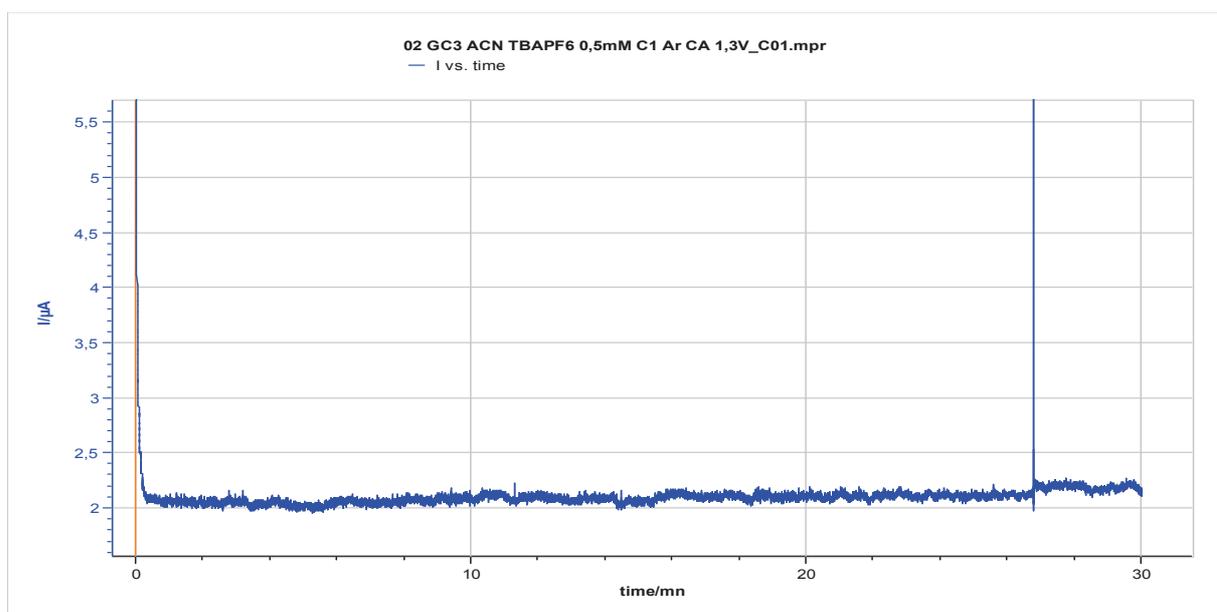


Figure 3.16: Chronoamperometry of C1 in ACN with 0.1 M of TBAPF₆ recorded at + 1.3 V.

The grafted electrode was washed in ACN and H₂O and then soaked in a blank solution of acetonitrile containing 0.1 M of TBAPF₆ saturated with Ar. As shown in Figure 3.17, the CV shape is similar to the one obtained after diazonium electro-grafting (Figure 3.9). Therefore, the electrode surface should be covered and the layer should be the same of diazonium electro-grafting. However, it is not possible to reproduce the oxidative grafting for C2 and C3.

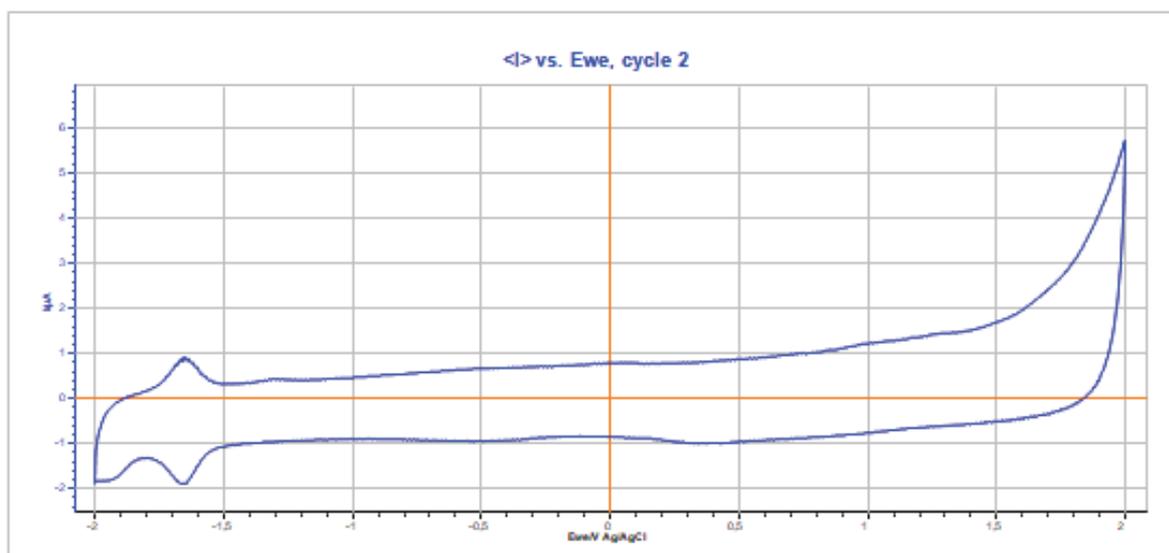


Figure 3.17: CV of Cl⁻ in ACN with 0.1 M of TBAPF₆ recorded at 100 mV s⁻¹ at glassy carbon electrode grafted (2nd cycle).

3.1.3 Re/pyta- N₃ complexes for click chemistry

Glassy carbon electrode surface can be functionalized by Re/pyta-N₃ complexes combining diazonium electro-grafting procedure with the click chemistry reaction.

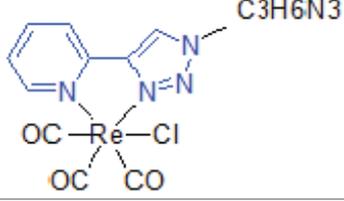
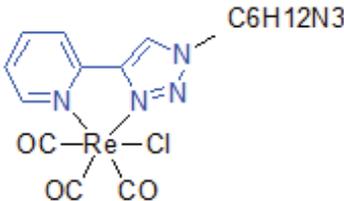
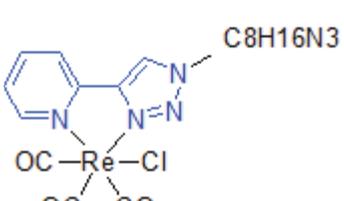
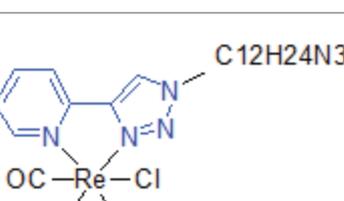
	Structure
C5	 C3H6N3
C6	 C6H12N3
C7	 C8H16N3
C8	 C12H24N3

Table 3.4: Re/pyta-N₃ complexes for click chemistry.

For this class of rhenium catalysts, the homogeneous behavior has been merely studied to test their catalytic activity. Thus, 0.5 mM of complex was dissolved in acetonitrile solution (0.1 M of TBAPF₆). CVs were performed under Ar and CO₂ atmosphere cycling potential from - 2 V to + 0.5 V at 100 mV s⁻¹. Figure 3.20, 3.21, 3.22 and 3.23 report the cyclic voltammograms of C5, C6, C7 and C8 respectively. Regarding CVs under Ar (blue curves), a first and single irreversible reduction peak is observed at - 1.7 V for each catalyst and it indicates the reduction of ligand. Saturating the system with CO₂ (red curves), a catalytic activity is visible because of the presence of the catalytic current. The cathodic peak is - 50 μA for C5, - 30 μA for C6, - 55 μA for C7, - 29 μA for C8. Comparing the catalysts in terms of the current values, the most active in solution is C7 because of the most negative catalytic current peak. Further investigations may be performed to covalently immobilize these complexes into different

surfaces. This step was not accomplished for this master thesis but the laboratory continues working in this strategy of immobilization.

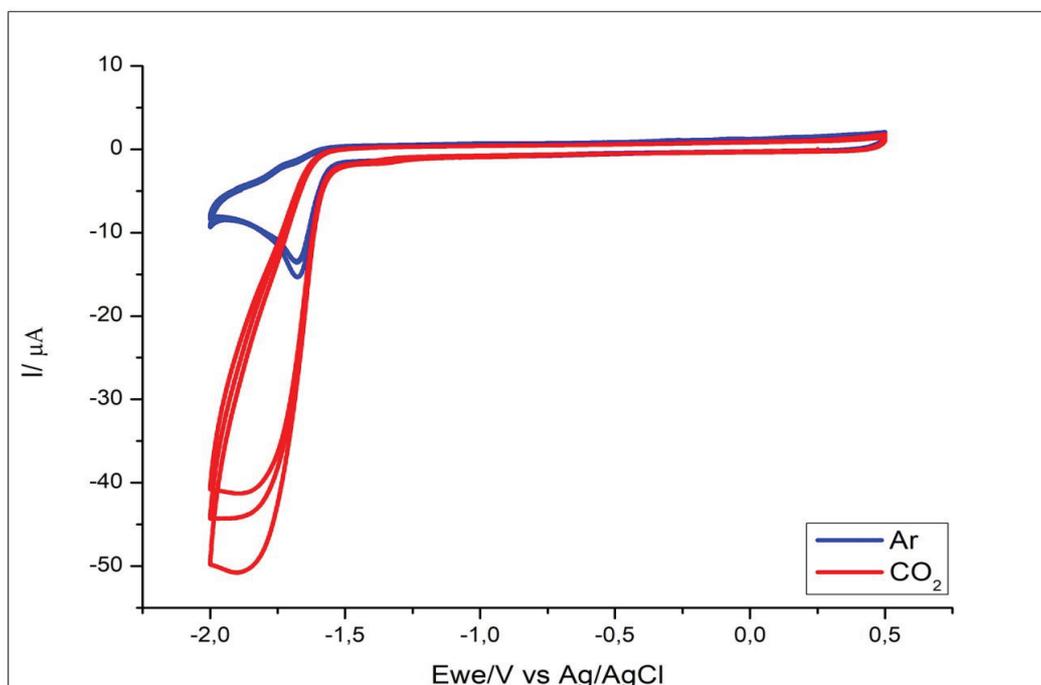


Figure 3.18: CVs of C5 in ACN with 0.1 M of TBAPF₆ under Ar (blue curve) and CO₂ (red curve) recorded at 100 mV s⁻¹ at glassy carbon electrode.

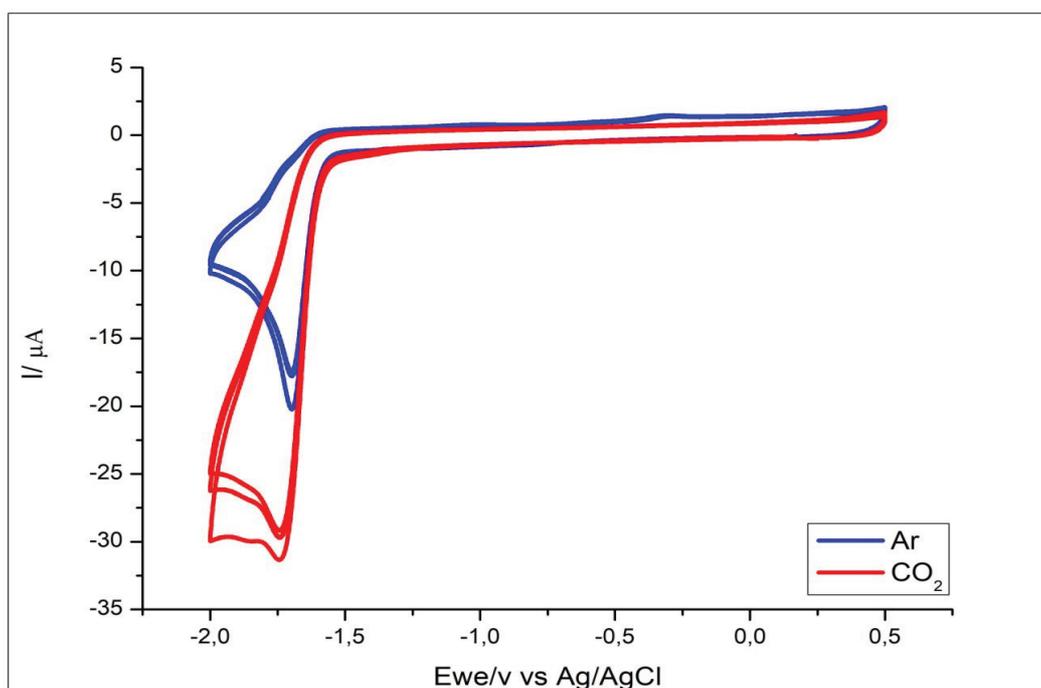


Figure 3.19: CVs of C6 in ACN with 0.1 M of TBAPF₆ under Ar (blue curve) and CO₂ (red curve) recorded at 100 mV s⁻¹ at glassy carbon electrode.

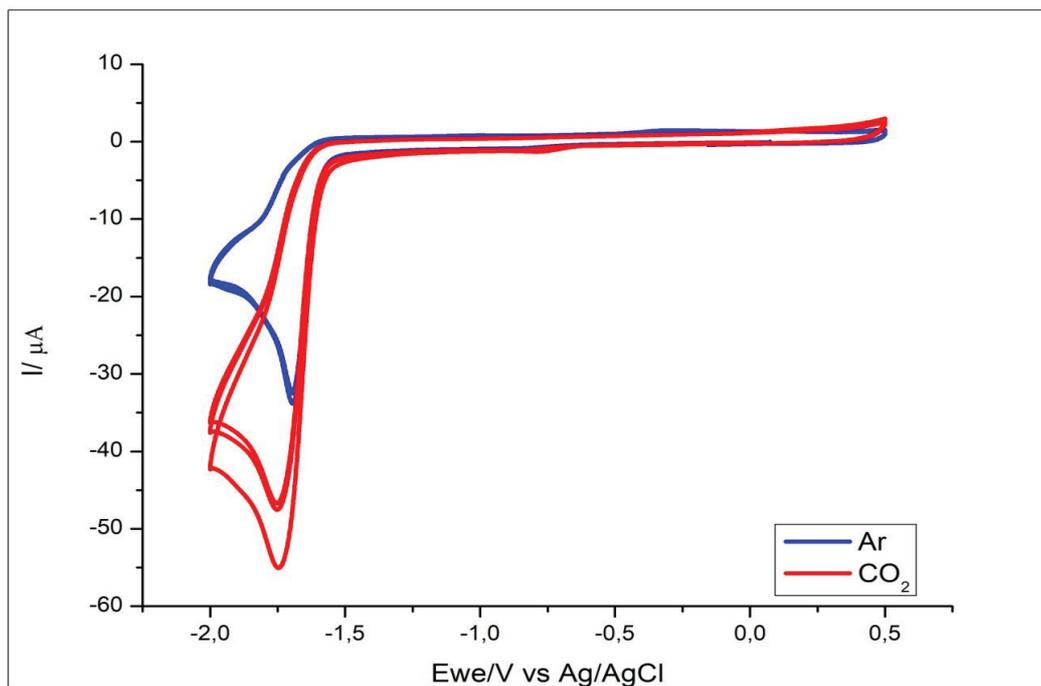


Figure 3.20: CVs of C7 in ACN with 0.1 M of TBAPF₆ under Ar (blue curve) and CO₂ (red curve) recorded at 100 mV s⁻¹ at glassy carbon electrode.

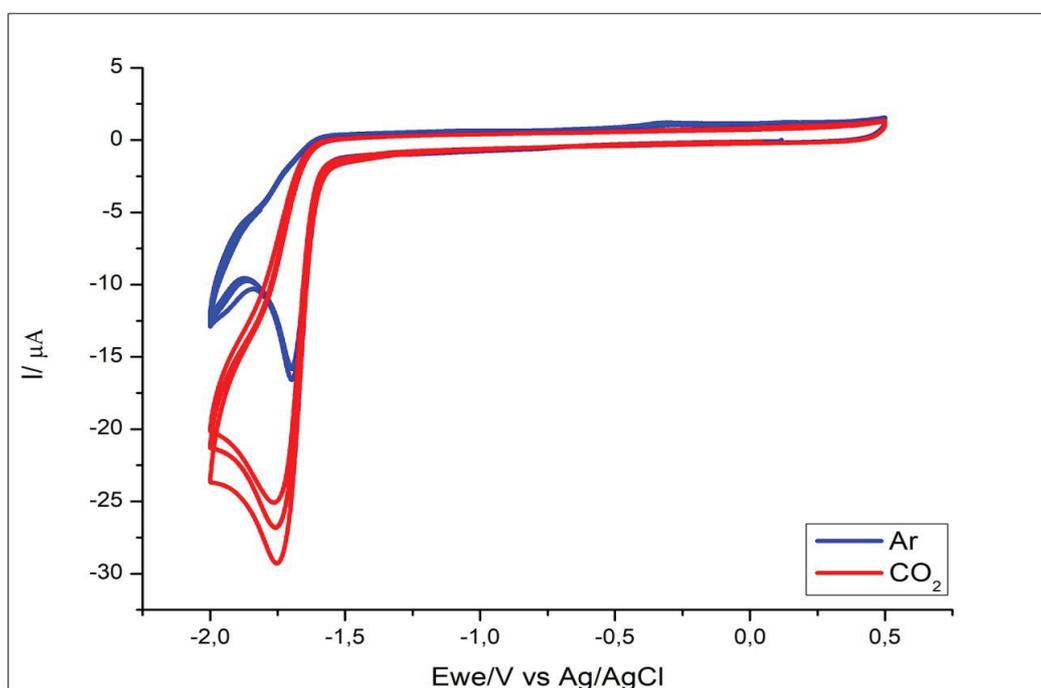


Figure 3.21: CVs of C8 in ACN with 0.1 M of TBAPF₆ under Ar (blue curve) and CO₂ (red curve) recorded at 100 mV s⁻¹ at glassy carbon electrode.

3.1.4 Re/pyta- COOH complex for peptide coupling

Thanks to a carboxyl functional group, Re/pyta-COOH complex can bind amide-functionalized carbon nanotubes on the glassy carbon surface. By a peptide coupling between the carboxylic group (-COOH) and the amine group (NH₂), the complex can be covalently fixed on the electrode surface. However, this condensation reaction of these two groups is kinetically very slow and thus needs from catalysts. This immobilization method was not properly investigated during this Master thesis.

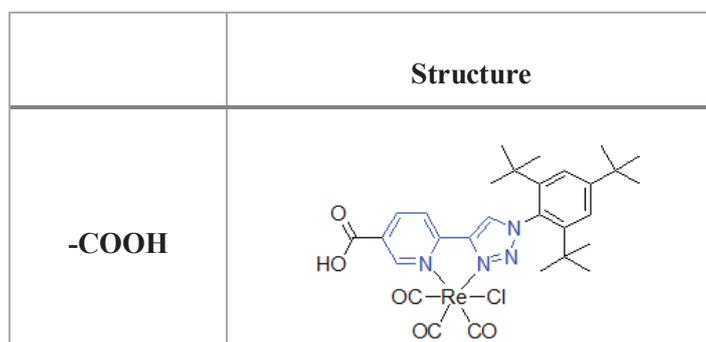


Table 3.5: Re/pyta- COOH complex for peptidic coupling immobilization

Thus, only some basic electrochemical studies of characterization and catalytic activity for CO₂ reduction were performed for this carboxylic derived complex. Cyclic voltammetry was carried out in ACN/ 0.1M of TBAPF₆ adding 0.5 mM of the catalyst. The system was saturated with Ar and, successively, with CO₂. CVs, reported in Figure 3.24, was done cycling the potential from -2 V to +0.5 V at 100 mV s⁻¹. Observing blue curves, the ligand reduction happens at -1.8 V and, degassing the system with carbon dioxide (red curves), a catalytic current is recorded.

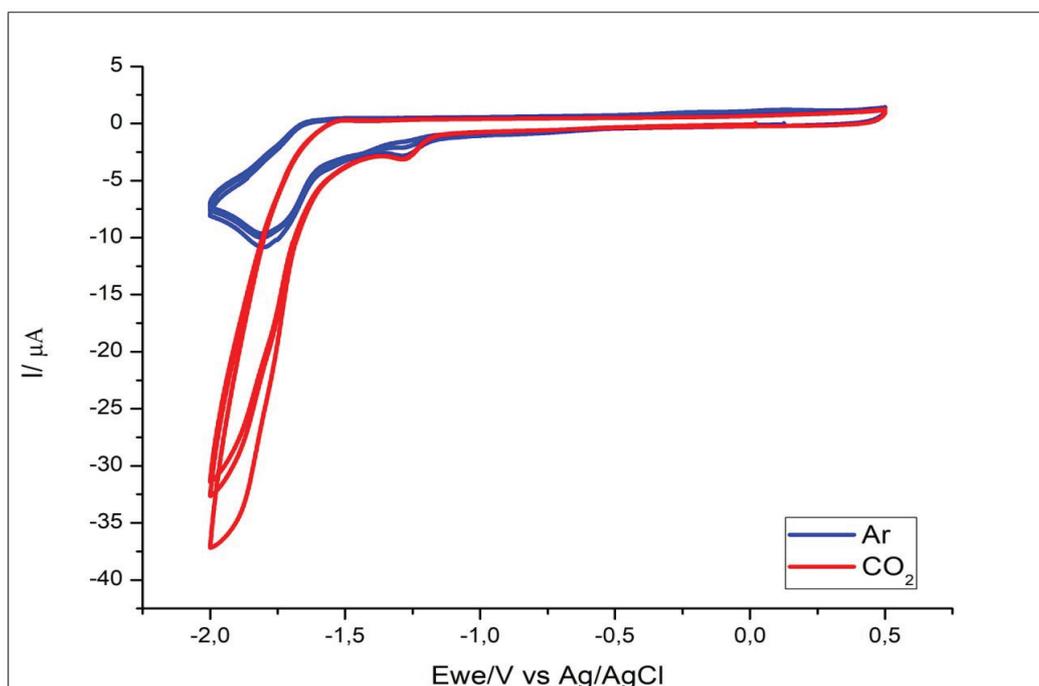


Figure 3.22: CVs of Re/pyta- COOH complex in ACN with 0.1 M TBAPF₆ under Ar (blue curves) and CO₂ (red curves) recorded at 100 mV s⁻¹ at glassy carbon electrode.

3.2 Non-covalent immobilization

3.2.1 Re/pyta- pyrene complexes for carbon nanotubes immobilization.

The last class of complexes is Re/pyta- pyrene complexes (Table 3.5), studied for a non-covalent immobilization on carbon nanotubes surface.

	Structure
VC-105	
VC-108	
Py/3-33	

Table 3.6: Re/pyta- pyrene complexes.

Their catalytic activity was studied in dimethylformamide (DMF) solution at 0.1 M of TBAPF₆ by cyclic voltammetry. The choice of DMF as solvent is due to the fact that this class of rhenium complexes is not soluble in acetonitrile, as the previous ones. Figure 3.26, 3.27, 3.28 show the VC-105, VC-108 and Py/3-33 voltammograms. Two reduction peaks are visible when the system is saturated with Ar (Figure 3.26 and 3.27, blue curves): -1.6 V and -1.8 V for VC-105 and -1.5 V and -1.9 V for VC-108. A single reduction process occurs at -1.66 V under Ar for Py/3-33. The first peaks are assigned to the ligand reduction. Saturating the system with carbon dioxide, each pyrene complex shows a catalytic current which indicates that CO₂ reduction is catalyzed. The most negative catalytic current is recorded for VC-108.

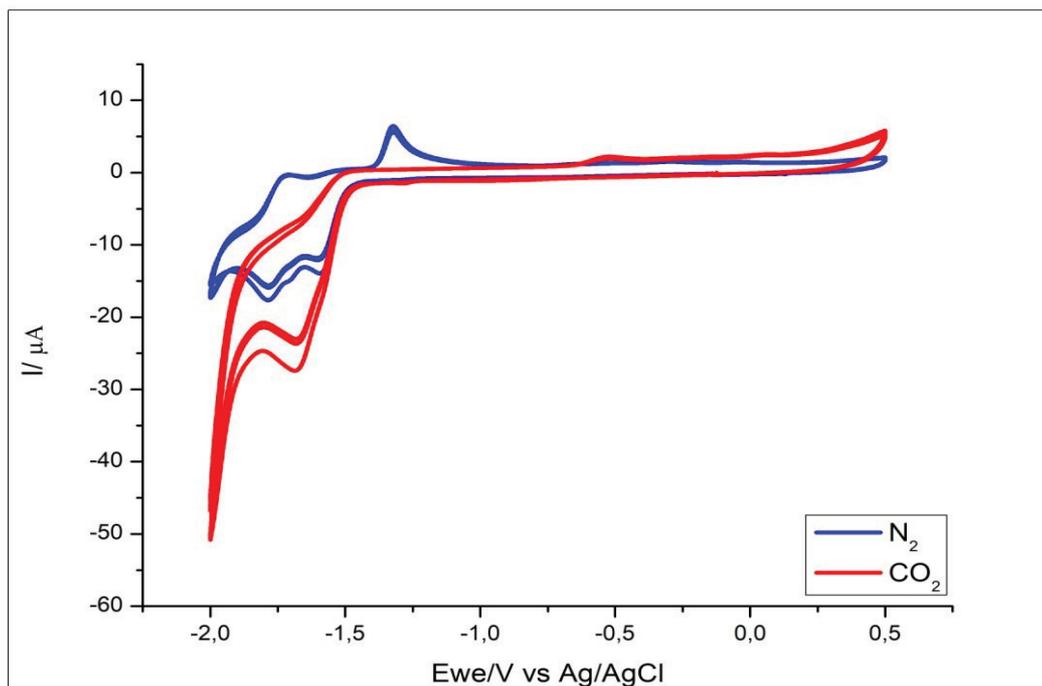


Figure 3.23: CVs of VC-105 in DMF with 0.1 M of TBAPF₆ under Ar (blue curve) and CO₂ (red curve) recorded at 100 mV s⁻¹ at glassy carbon electrode.

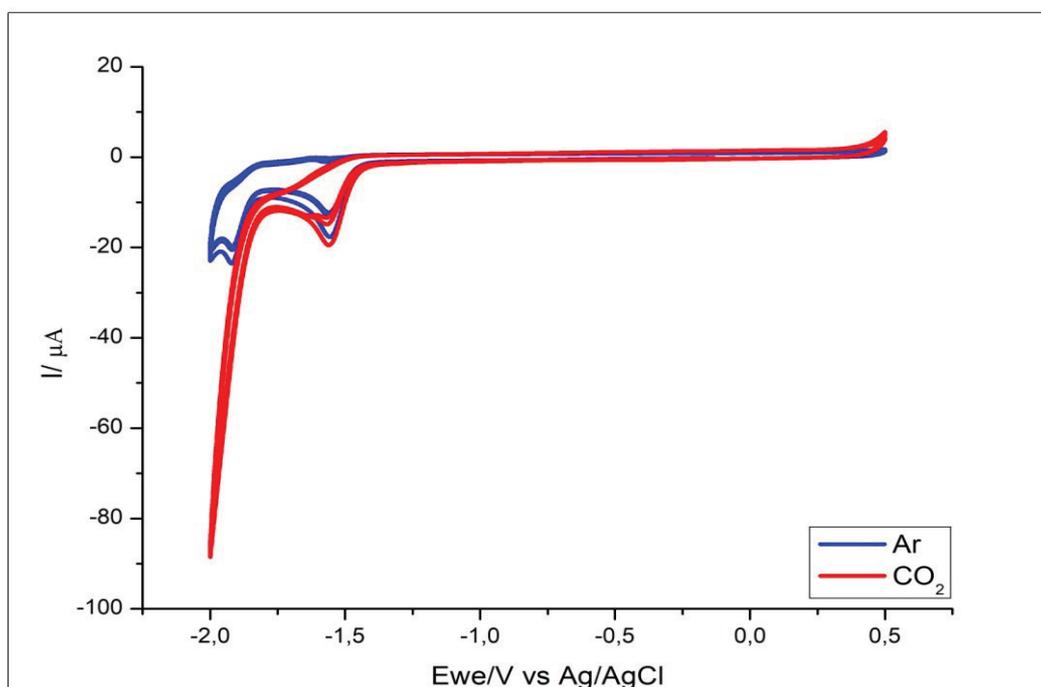


Figure 3.24: CVs of VC-108 in DMF with 0.1 M of TBAPF₆ under Ar (blue curve) and CO₂ (red curve) recorded at 100 mV s⁻¹ at glassy carbon electrode.

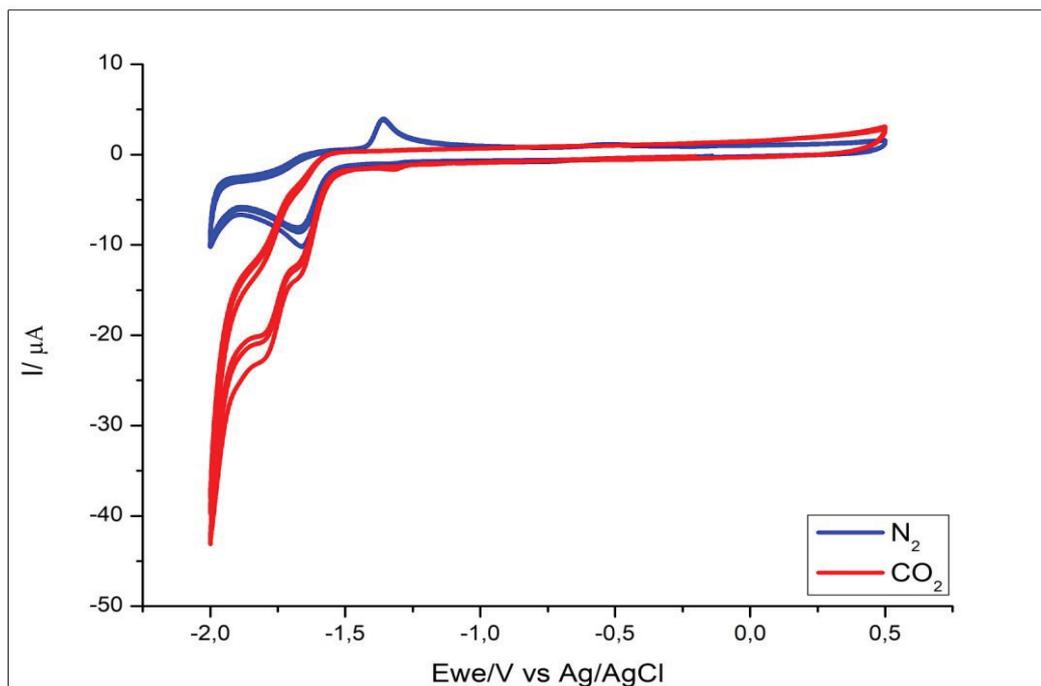


Figure 3.25: CVs of Py/3-33 in DMF with 0.1 M of TBAPF₆ under Ar (blue curve) and CO₂ (red curve) recorded at 100 mV s⁻¹ at glassy carbon electrode.

As shown in Figure 3.29, 3.30 and 3.31, the addition of TFE, as proton source, helps the carbon dioxide reduction. Under CO₂, the trifluoroethanol was added in 5 % (red curves), 10 % (green curves) and 20 % (purple curves) v/v and it is easy to observe an increase in the catalytic current if compared to the case without any proton source.

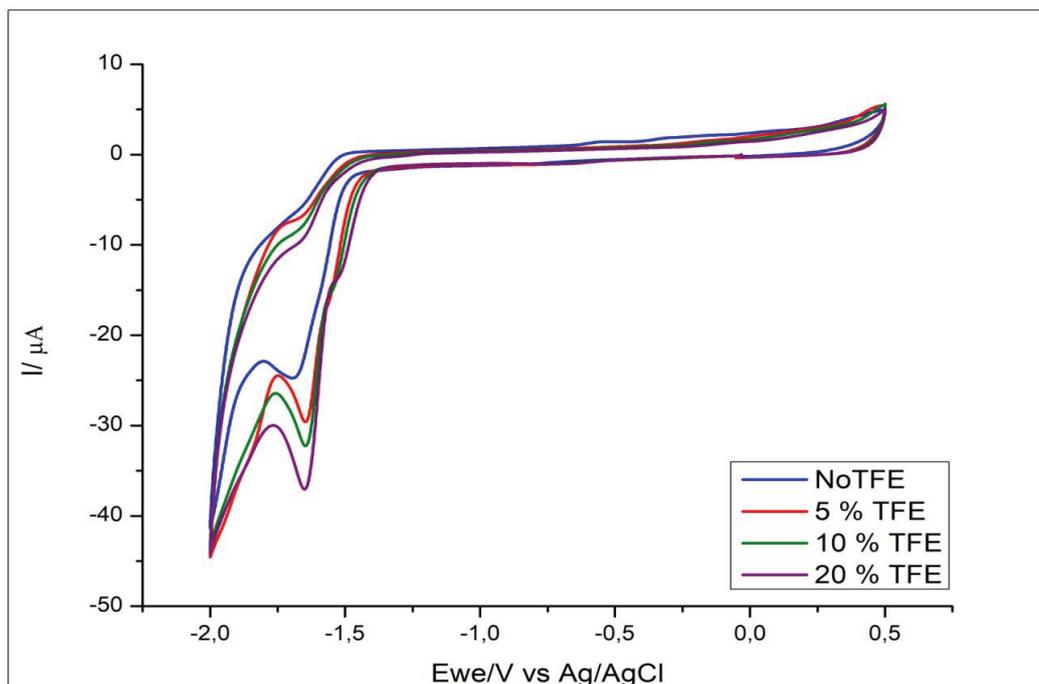


Figure 3.26: CVs of VC-105 in DMF with 0.1 M of TBAPF₆ under CO₂ (blue curve) adding 5 % of TFE (red curve), 10 % of TFE (green curve) and 20 % of TFE (purple curve) recorded at 100 mV s⁻¹ at glassy carbon electrode.

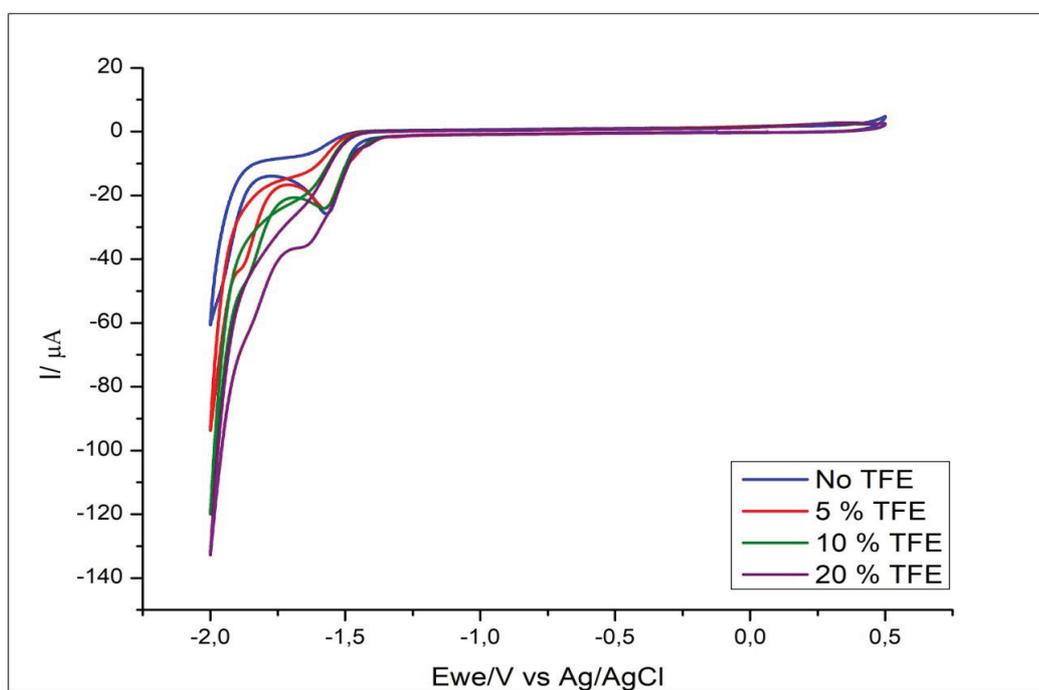


Figure 3.27: CVs of VC-108 in DMF with 0.1 M of TBAPF₆ under CO₂ (blue curve) adding 5 % of TFE (red curve), 10 % of TFE (green curve) and 20 % of TFE (purple curve) recorded at 100 mV s⁻¹ at glassy carbon electrode.

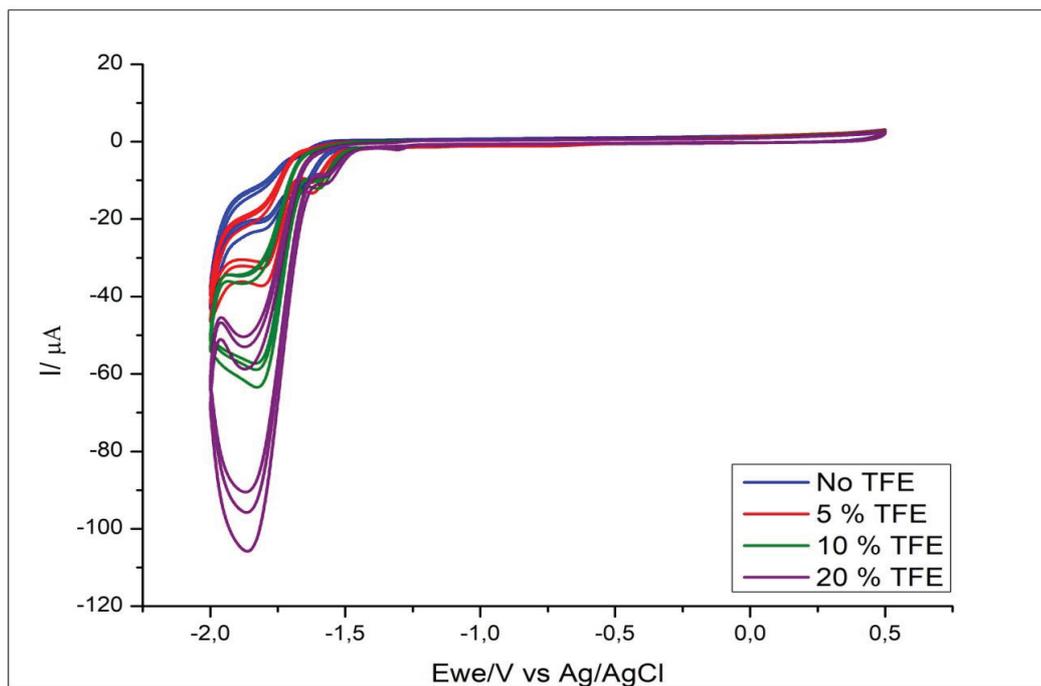


Figure 3.28: CVs of Py/3-33 in DMF with 0.1 M of TBAPF₆ under CO₂ (blue curve) adding 5 % of TFE (red curve), 10 % of TFE (green curve) and 20 % of TFE (purple curve) recorded at 100 mV s⁻¹ at glassy carbon electrode.

For the heterogeneous case, the rhenium pyrene complexes was directly immobilized onto CNT via adsorption, as reported in the previous section. Firstly, the carbon nanotubes modified electrode was characterized by cyclic voltammetry and compared to a bare electrode characterization. Figure 3.32 and 3.33 reports the cyclic voltammogram in ACN/0.1 M of TBAPF₆ solution under Ar and CO₂ atmosphere for a bare electrode and a CNT-functionalized one respectively. The main difference is a higher capacitive current due to the presence of carbon nanotubes and their larger surface area.

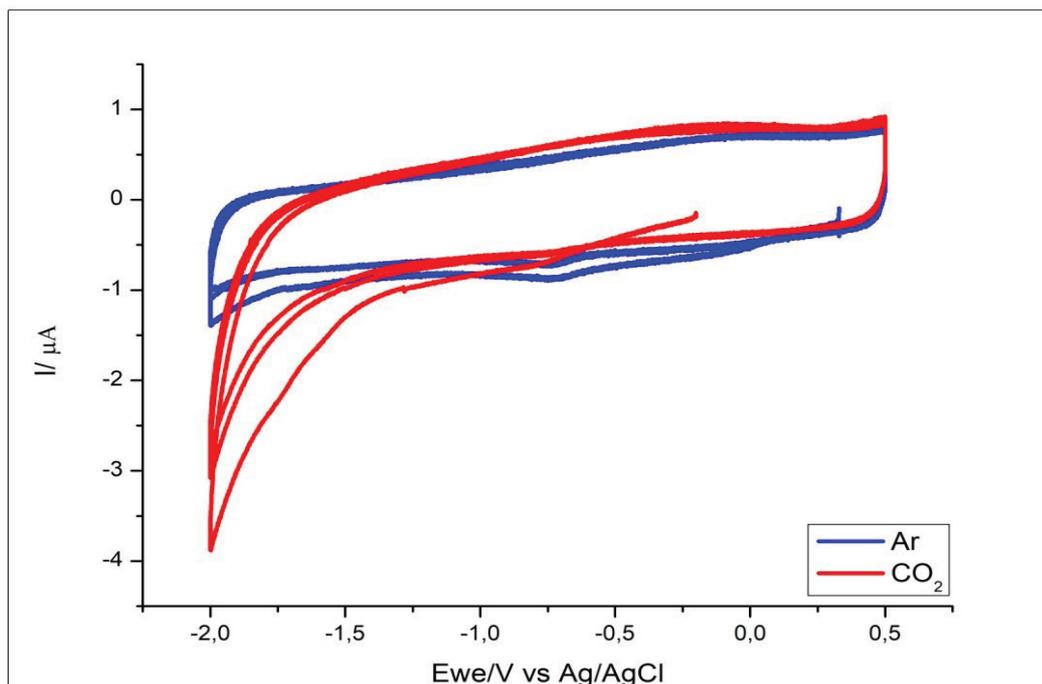


Figure 3.29: CVs of blank solution of ACN with 0.1 M of TBAPF₆ under Ar (red curve) and CO₂ (blue curve) recorded at 100 mV s⁻¹ at glassy carbon electrode.

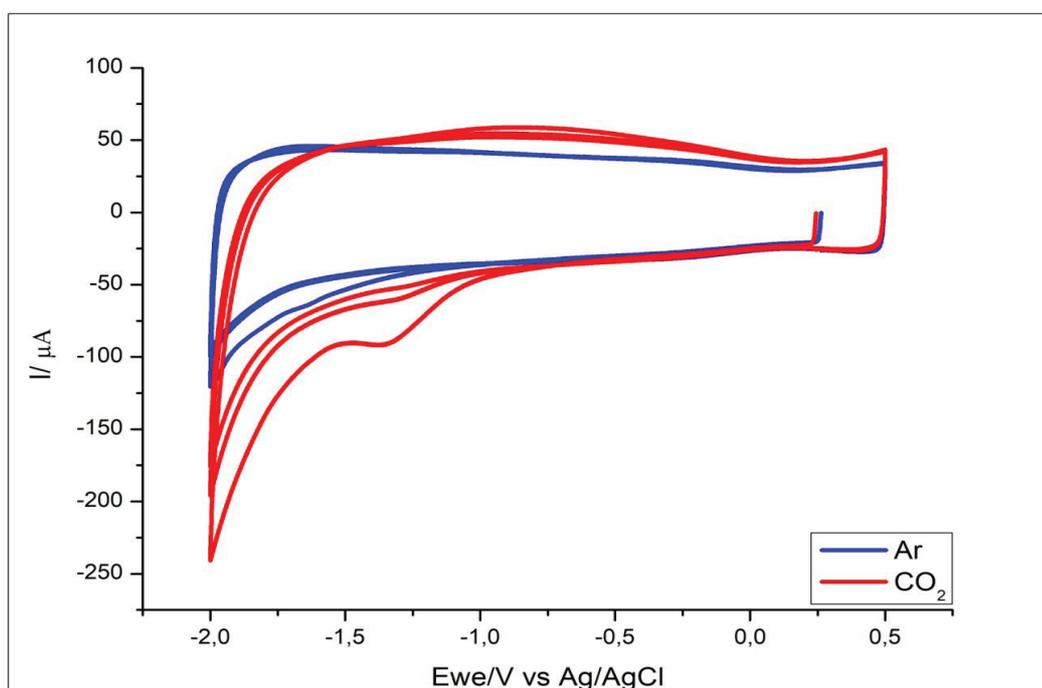


Figure 3.30: CVs of blank solution of ACN with 0.1 M of TBAPF₆ under Ar (red curve) and CO₂ (blue curve) recorded at 100 mV s⁻¹ at glassy carbon electrode modified with SWCNTs.

Secondly, following the procedure reported in the previous section, the catalysts was fixed on CNTs surface via pyrene unit. Cyclic voltammograms are reported in Figure 3.34, 3.35 and 3.36. The analysis was conducted in acetonitrile solution at 0.1M of TBAPF₆ and the results

demonstrate that there is a reduction process under Ar (blue curves) at - 1.7 V which does not occur after the first cycle. The potential of the peak is similar for VC-105, VC-108 and Py/3-33. In the case of the system purged with CO₂ (red curves), the catalyst effect is showed by a catalytic current and a lower onset potential around - 1.4 V.

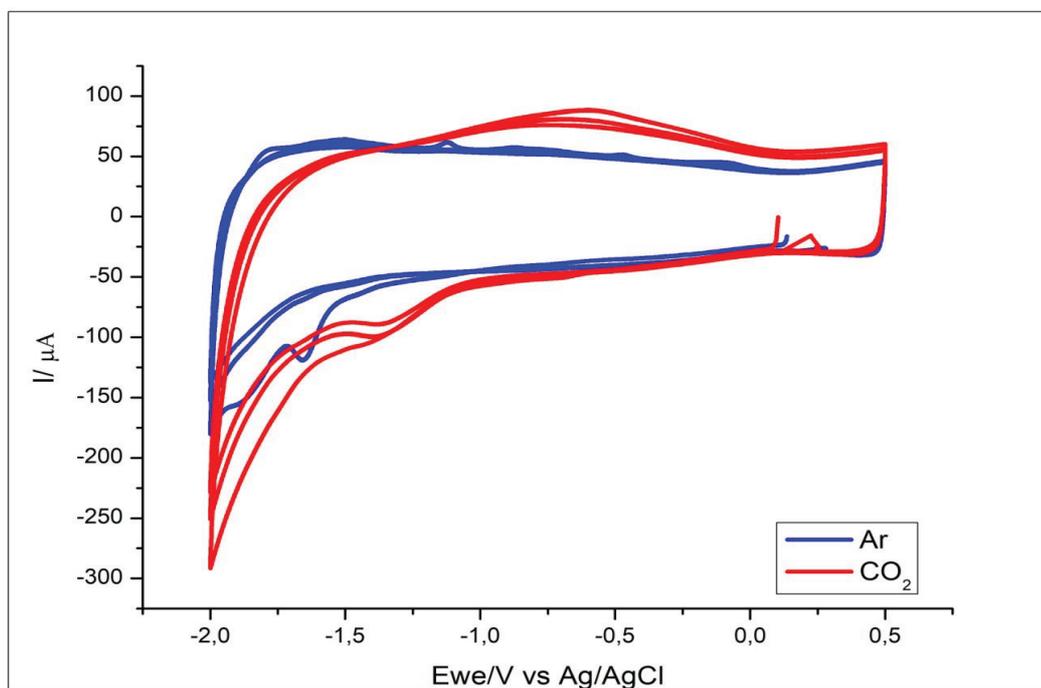


Figure 3.31: CVs of VC-105 immobilized on CNTs surface in ACN with 0.1 M of TBAPF₆ under Ar (red curve) and CO₂ (blue curve) recorded at 100 mV s⁻¹ at glassy carbon electrode.

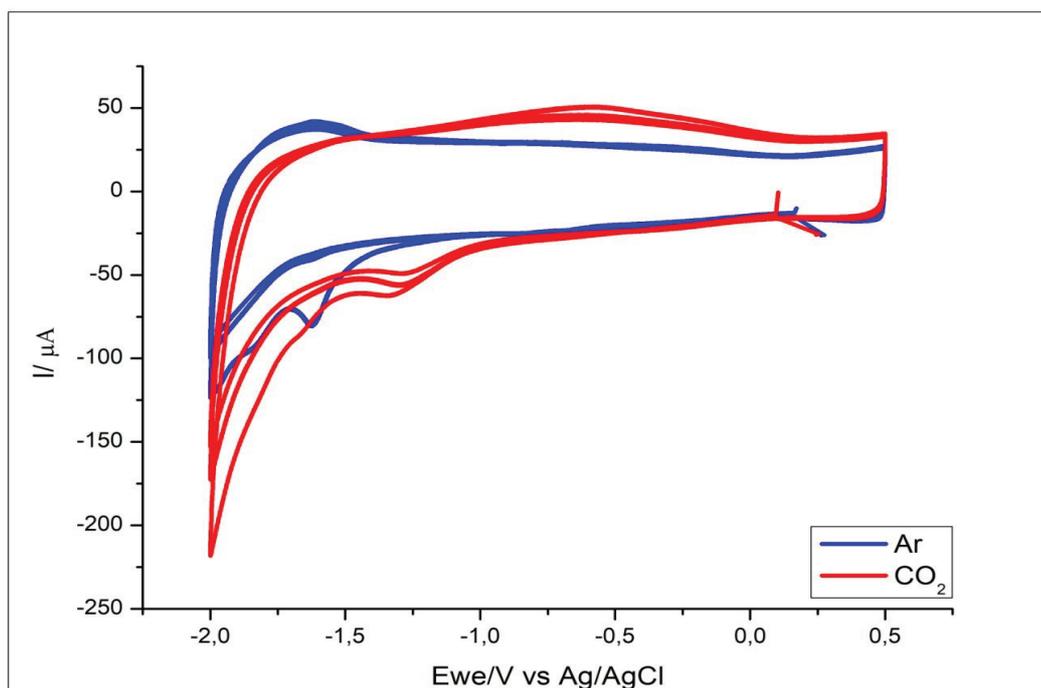


Figure 3.32: CVs of VC-108 immobilized on CNTs surface in ACN with 0.1 M of TBAPF₆ under Ar (red curve) and CO₂ (blue curve) recorded at 100 mV s⁻¹ at glassy carbon electrode.

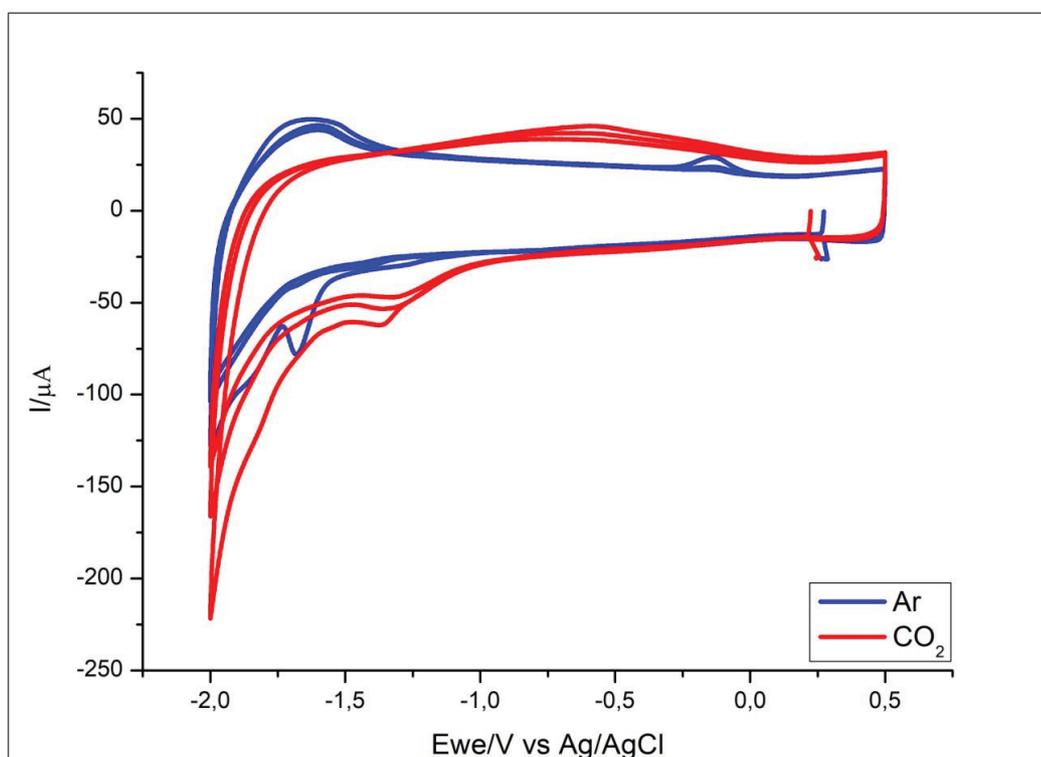


Figure 3.33: CVs of Py/3-33 immobilized on CNTs surface in ACN with 0.1 M of TBAPF₆ under Ar (red curve) and CO₂ (blue curve) recorded at 100 mV s⁻¹ at glassy carbon electrode.

Using the set-up of Figure 2.5, electrolysis analysis was performed at - 1.7 V, as fixing potential, for 2 hours. The electrolyte solution was acetonitrile containing 0.1 M of TBAPF₆ and the system was saturated with CO₂. Figure 3.37 shows the current trend over the time for the CNTs.-modified electrode (blue curve), and for the VC-105/CNTs (red curve), the VC-108/CNTs (green curve) and the Py/3-33/CNTs (purple curve) functionalized electrode. The charge trend over the time is reported in Figure 3.38.

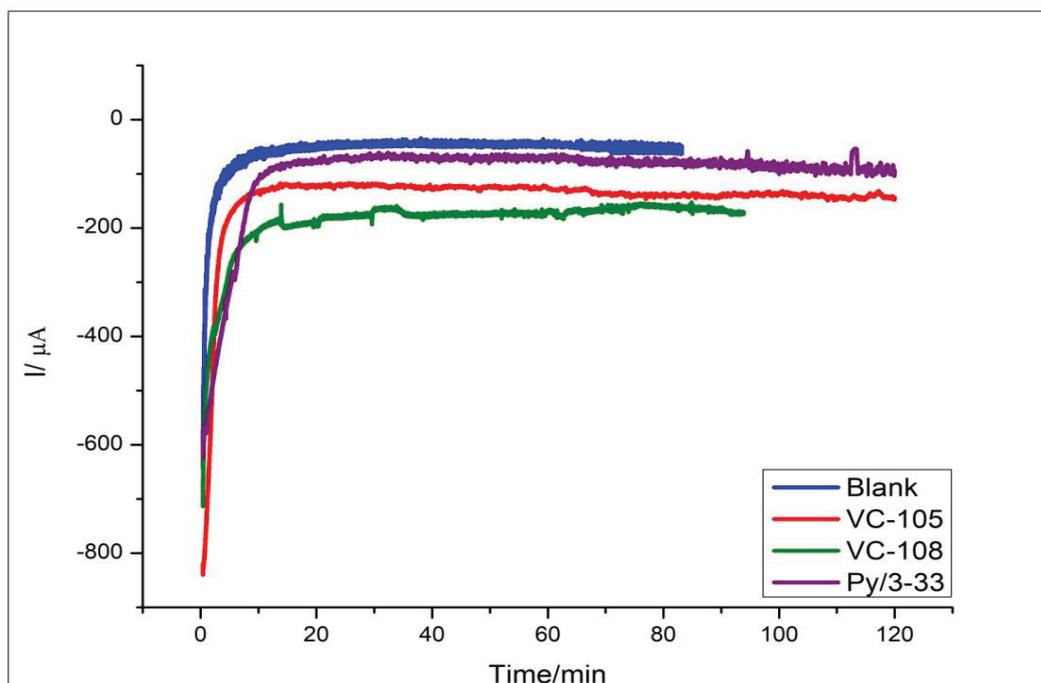


Figure 3.34: CPE (Current vs Time) in ACN with 0.1 M of TBAPF₆ purged CO₂ recorded at grafted glassy carbon electrode modified by CNTs: blank (blue curve), VC-105 (red curve), VC-108 (green curve), Py/3-33 (purple curve).

Observing Figure 3.37, the current intensity remains approximately constant after 10 minutes and this result indicates the stability of the attached catalyst. Depending on the current value, it is also possible to identify the catalyst with the best affinity for carbon dioxide electro-reduction. In this context, Py/3-33 records a stable current value (- 250 μA) more negative than VC-105 and VC-108.

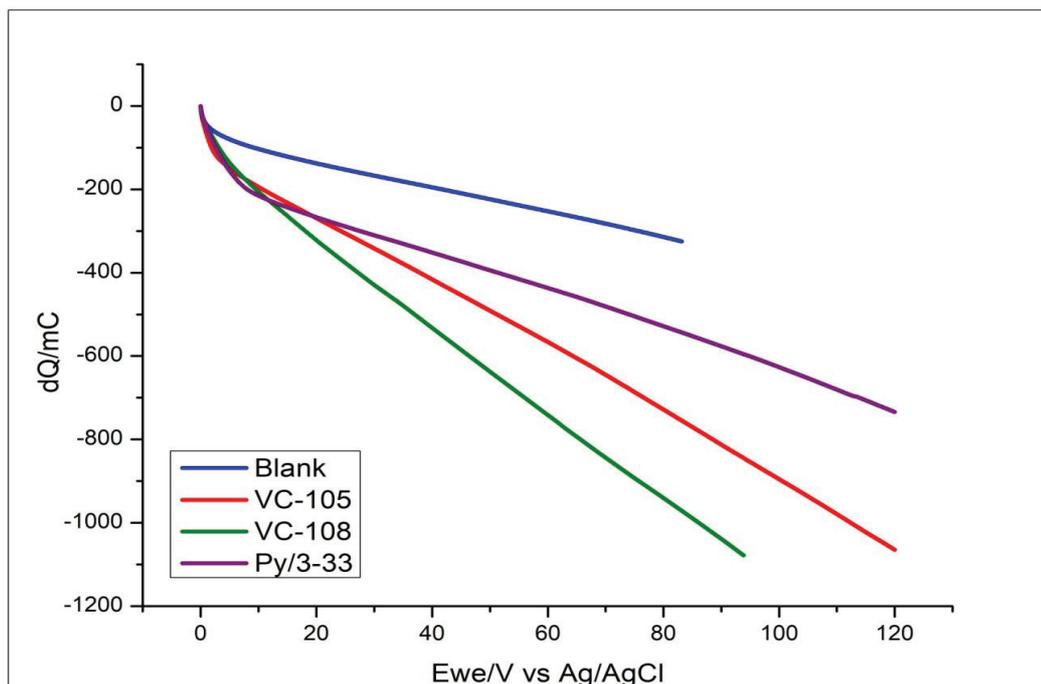


Figure 3.35: CPE (Charge vs Time) in ACN with 0.1 M of TBAPF₆ purged CO₂ recorded at grafted glassy carbon electrode modified by CNTs: blank (blue curve), VC-105 (red curve), VC-108 (green curve), Py/3-33 (purple curve).

As demonstrated by gas chromatography results, reported in Table 3.6, CO and H₂ are the main products of the CO₂ electro-reduction, catalyzed by rhenium pyrene complexes in heterogeneous phase. Any formate was found. In the absence of the catalyst, hydrogen production is the main reaction producing: 0.6 μmol after 2 hours of CPE. Comparing the catalysts, it is easy to see that Py/3-33 gives more CO than VC-105 and VC-108, as it is also confirmed by the value of the current during the electrolysis. The small amount of the H₂ moles produced after 2 hours indicates that it has a good selectivity for carbon monoxide evolution (FE = 28 % for CO and CO/H₂ = 2). The CO production trend during the CPE time is reported in Figure 3.39. The VC-105 catalyst reaches the maximum CO production after 10 minutes of the CPE and then it remains in a plateau regime (constant CO amount). In the case of VC-108, although it showed the best performance for the carbon dioxide reduction in homogeneous conditions, it gives a small amount of CO when compared to the others. In the end, the green curve proves the catalytic activity of Py/3-33 complex which produces the maximum amount of CO after 30 minutes, meaning that it is slower than VC-105, but in the other hand, Py/3-33 is the most selective for carbon monoxide production.

	$\mu\text{mol CO}$	$\mu\text{mol H}_2$	$I/\mu\text{A}$	dQ/C	FY CO	FY H ₂
Blank	0,20	0,6	-35	-0,324	25%	70%
VC-105	0,60	0,7	-125	- 1,064	24,8%	22 %
VC-108	0,30	0,48	-175	- 1,08	17 %	11 %
Py/ 3-33	1,03	0,48	-250	- 1,42	28,2 %	13 %

Table 3.7: Amount of CO and H₂ , charge and Faradaic yield after 2 hours of CPE.

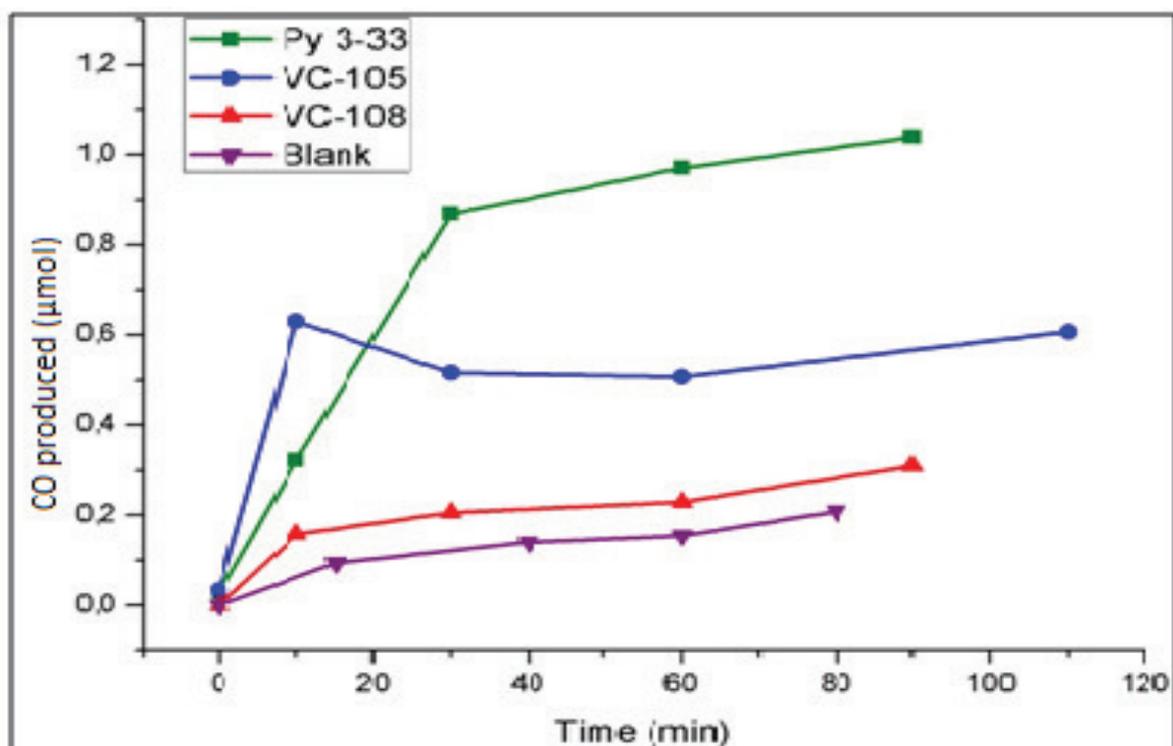


Figure 3.36: Amount of CO produced after 2 hours of CPE by blank (purple curve), VC-105 (blue curve), VC-108 (red curve) and Py/3-33 (green curve).

4. Conclusions

The current challenge to decrease the greenhouse effect and to produce added-value chemicals or fuels using renewable energy sources generates a continuing interest in catalyst development for CO₂ electro-reduction. Regarding carbon monoxide production, many non-noble catalysts have been studied in homogeneous conditions although there are only a few examples of studies of these complexes immobilized in electrode surfaces. In this thesis, a new series of rhenium pyta tricarbonyl complexes has been investigated to catalyze electrochemical CO₂ conversion. Each Re/pyta complex was synthesized following the procedure reported in the second section: four several classes of rhenium complexes were obtained and were tested for different immobilization methods. Re/pyta- aniline complexes were used for diazonium electro-grafting and oxidative grafting. They displayed similar CV features and the same potential peak for rhenium reduction in solution, but CO₂ effect was more visible for the one with the shorter side chain (C1). Their immobilization on the glassy carbon surface by diazonium electro-grafting works, was demonstrated by the linear trend of the current over the scan rate. However, the catalyst layer disappeared after carbon dioxide cycling. Instead, during controlled potential electrolysis experiment, the layer may remain attached on the electrode surface, since carbon monoxide and hydrogen were continuously produced for 2 hours and the current obtained was constant. CO and H₂ were the only products of the electro-catalytic reaction. After 2 hours of CPE performance, C1 proved to be the catalyst which gave more CO than the others, promoting also hydrogen evolution. In the other hand, C3 was more selective for carbon monoxide production with the highest Faradaic efficiency around 47 %. Although, C2 showed an inactivity after 30 minutes of electrolysis. The second approach for the grafting of the rhenium pyta aniline catalysts was the oxidative grafting. It seemed to work better for C1 than for C2 and C3 and the C1 layer resulted similar to reduction by C1 diazonium electro-grafting. This type of immobilization should be improved for C2 and C3; adding a proton source could be a solution to activate them, because they have to be neutralized. Re/pyta- N₃ complexes have been studied only in homogeneous conditions and C7 is the one which recorded the highest catalytic current under carbon dioxide atmosphere. Click chemistry combined with diazonium electro-grafting could be a way to immobilize this class of catalysts on the GCE surface. Furthermore, concerning carbon nanotubes immobilization by a peptide coupling, the results have not yet been explored. In the end, the homogeneous behavior of Re/pyta-pyrene complexes has been examined. Their catalytic activity was proved by cyclic voltammetry; the potential of the first reduction peak was similar for each complex and associated to the ligand reduction; the second irreversible reduction peak was unknown. Observing the recorded catalytic current, CO₂ effect was remarkable. This catalysts group was fixed on the electrode surface by an interaction between pyrene unit and carbon nanotubes. CNTs immobilization method on the GCE surface works and it was confirmed by the huge reported capacitive current in the voltammogram; it is due to a highest surface area. Binding the catalyst on the carbon nanotubes structure, the onset potential is shifted to more positive values under CO₂ saturated atmosphere. During CPE performances, a stable current was recorded and Py/3-33 reached the most negative value. As a matter of fact, it was slower than VC-105 and VC-108, but it produced more CO with a Faradaic efficiency of 28 %. An improvement of the immobilization parameters, such as immobilization time, catalyst concentration, drop volume, ecc. should be performed to find their optimum combination. Therefore, this study could be a starting point to better understand and improve the catalytic activity and selectivity of this new class of CO₂ reduction catalysts and to investigate which immobilization method on the GCE surface is the most efficient.

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