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Electrochemical Tuning of CO₂ Reactivity in Ionic Liquids Using Different Cathodes: From Oxalate to Carboxylation Products

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Abstract: There is currently quite a lot of scientific interest in carbon dioxide (CO₂) capture and valorization with ionic liquids (ILs). In this manuscript, we analyze the influence of the potential applied, the nature of the cathode and the electrolyte using different organic mediators, such as nitro or cyano aromatic derivatives, to promote the electrochemical activation of CO₂. An electrocatalytic process using a homogeneous catalysis is seen when nitroderivatives are used, yielding to oxalate in organic electrolytes and ILs. Turnover frequency (TOF) values and Faraday efficiencies were slightly higher in *N,N'*-dimethylformamide (DMF) than in ILs probably due to the viscosity of the electrolyte. The use of cyano derivatives allows to tune the electrochemical reactivity in function of the reduction potential value applied from electrocarboxylated products (via a nucleophile-electrophile reaction) to oxalate. These electrochemical reactions were also performed using three different cathodes, organic electrolytes and ionic liquids. The use of copper, as a cathode, and ionic liquids, as electrolytes, would be a cheaper and greener alternative for activating carbon dioxide.

Keywords: CO₂; electrochemistry; ionic liquid; catalysis; carboxylation; green chemistry

1. Introduction

Nowadays methane, nitrous oxide and carbon dioxide (CO₂) emissions represents approximately 98% of the total greenhouse gas (GHG) inventory worldwide [1–3], and their share are expected to increase this twenty-first century. CO₂ represents the most important GHG, which represents approximately the 77% of the global GHG emissions (considering its global warming potential) worldwide. Moreover, the change in atmospheric CO₂ concentration has been considered the most important driver of global warming. In 2019 carbon dioxide emissions from energy stagnated at 33 Gt, which are mainly due to anthropogenic activities. Besides, it is expected to increase to 40.3 Gt by 2030 and to 50 Gt by 2050, if proper measures are not taken [4–7].

In the last decade, new concepts have been developed as a suitable approaches for facing the challenges of the current global scenario; so biomimetic [8] and circular economy models have been formulated. All the approaches involve a first capture step for an efficient removal of CO₂ from common points sources prior to the release of gases into atmosphere [9–12].

Carbon capture and storage (CCS) approaches include planning the confinement of CO₂ into depleted oil and gas wells, deep oceans, and aquifers [13]. Capture approaches based on chemical absorption and desorption using an aqueous amine solution are also one of the most promising option for separating CO₂ from fossil-fuel-derived flue gas due to its simple operation, high absorption efficiency, cost-effectiveness and maturity [14,15]. However, all these strategies only partially solve the problem, so approaches to recover valuable products from its conversion through a circular economy

vision are highly desirable [16,17]. In this sense, some conversion routes are designed for the reuse of fuels, especially when inexpensive renewable energy processes are available.

New approaches that transform CO₂ in fine chemicals or value-added products are also being deeply investigating. The remunerability of the product is much higher and can economically support the development of the technologies involved. However, the volume of the potential market of these fine chemicals can hardly match with the volume of CO₂ emissions, needing the development of a network of parallel CCU technologies. Hence, different strategies, including biological methods, have been developed either for directly producing reduced products (i.e., carbonic anhydrase, hydrogenation of CO₂ to formate, reduction of CO₂ to methane, CO₂ conversion into methanol by enzyme cascade) or to store CO₂ in biomass (e.g., algae) [18–20]. The photocatalytic reduction approaches also allow to synthesize a wide spectrum of CO₂ reduction products, such as HCOOH, HCHO, CH₃OH, or CH₄, and can be effectively used by using visible responsive materials [21–27]. Adsorption, CO₂ activation and further reduction to produce value-added products are crucial steps for photocatalytic processes. Sharma et al. reported a combined theoretical and experimental study describing the selective reduction of CO₂ into methane through a robust visible-light photocatalyst based on single-phase ternary sulfide (CTS) [28]. Zhou et al. proposed the use of aqueous suspensions of cubic ZnS nanocrystals for the photocatalytic reduction of CO₂ into formate [29]; and the development of heterostructures, such as Cu₂O/TiO₂, for artificial photosynthesis [30].

Chemical catalytic strategies for CO₂ reduction have been proposed mainly based on the Sabatier reaction [31]. Finally, it is worthy to highlight that in the last years, it has been also reported that the development of electrochemical technologies to capture and transform CO₂ into high-added value products is a suitable and green way for activating CO₂ compared to others Carbon Capture, Utilization and Storage (CCUS) strategies [32].

Direct carboxylation of carbon nucleophile using CO₂ as an electrophile is a straightforward route to prepare carboxylic acids. The main drawback associated to this process is related to the use of toxic reagents and the production of a large amounts of waste [33]. For instance, the conventional route for synthesizing 6-aminonicotinic acid from the corresponding nitriles involves low yields, hazardous chemicals (such as cyanide and ammonia gas) and high temperatures [34–36]. Nevertheless, using organic electrochemistry techniques improve environmental conditions [37–50]. One of the most widely used approaches for valorizing CO₂, is to use organic halides with electrochemical techniques, which makes it possible to activate the CO₂ (Scheme 1, Equations (1)–(4)); In a first step, a one electron transfer process generates the organic radical anion, which later converts to an anion through a second reduction electron transfer and a halide anion. The key to this approach relies on the reduction potential value of the organic halides and the stability of the organic anion formed after the reduction process [51–65].

The development of selective electrocatalysis processes for the reduction of carbon dioxide (CO₂) to yield C₁ products (such as CO (2e[−]), or higher C_n products) would allow the use of CO₂ as a carbon feedstock (Scheme 1). Nevertheless, it is necessary to overcome high-energy barriers for the direct reduction of CO₂, which commonly implies reduction potential values significantly more negative than the corresponding thermodynamic reduction potential value of CO₂. In this sense, different types of electrodes have been studied for direct reduction of CO₂. These cathodes are classified based on the nature of the main product obtained in the electrochemical process in aqueous and non-aqueous supporting electrolytes [66]. Moreover, it has also been developed other kinds of modified or doped electrodes (with immobilized enzymes, nanoparticles or metallic oxides) to catalyze CO₂ direct reduction [67–69]. Hence, the improvement of electrocatalytic processes could lower overpotential requirements while maintaining appropriate catalytic rates and selectivity [70–91].

Scheme 1. Electrochemical strategies to valorize CO₂.

One of the most common techniques to analyze electrocatalysis is cyclic voltammetry, which provides direct and rapid information regarding the relationship between driving force (i.e., overpotential) and catalytic turnover (i.e., current) compared to rather complicated alternative methods monitored by spectroscopy or other means. However, understanding detailed mechanistic schemes behind voltammograms is quite challenging due to complicated and intertwining processes, such as mass transport, electron transfer, chemical reaction and interfacial chemistry between electrode and reactants. In this sense, developing the foot of the wave analysis (FOWA) of cyclic voltammetry by Savéant and Costentin has provided a feasible method to benchmark molecular electrocatalysts by turnover frequency (TOF) and turnover number (TON) [92–96].

Molecular catalysts are an attractive option owing to the high degree of tunability of electronic and geometric parameters, which allows for systematic reactivity studies that can lead to new catalyst design guidelines. The well-defined structure of the catalytic sites also allows the establishment of a precise structural model for better analysis of the multiple proton-coupled electron transfer processes involved in CO₂ reduction and better understanding of the CO₂ reduction mechanism. For example, Leung et al. proposed a mechanism for CO production using Co-based porphyrins [97,98], where the [Co(P)–(CO₂)]^{2–} intermediate will be protonated to form [Co(P)–(COOH)][–]. Later, it will decompose to provide CO. Koper and co-workers proposed a different mechanism [99], where the formation of the CO₂[–], anion intermediate, will be protonated yielding to [Co(P)–(COOH)]⁰ intermediate. Then, [Co(P)–(COOH)]⁰ will decompose to CO. Finally, Yao et al. proposed a pre-activation process to form a local proton source could facilitate CO₂ reduction [100].

The electrocatalysts participates in an electron transfer reaction (on the electrode surface) and facilitates acceleration of a chemical reaction. Both electron transfer and chemical kinetics must be fast for an efficient electrocatalyst. In addition, an optimal electrocatalyst must display a good thermodynamic match between the redox potential (E^0) for the electron transfer reaction and the chemical reaction that is being catalyzed (in this work; CO₂ reduction). Chemical tuning of the electrocatalyst can optimize these factors. A general approach for an electrocatalytic system is given in Scheme 2.

The electrocatalytic activity can be analyzed in terms of in cyclic voltammetry (CV). In a CV under a dry inert atmosphere, an electrocatalyst should show a reversible redox couple. Upon addition of the reagent which is catalyzed (i.e., CO₂), the diffusion limited current should increase significantly, while the potential shifts anodically, and the reversibility in the return oxidation wave is lost due to the chemical reaction between reagent and electrocatalyst. Electrocatalyst offer critical solutions to lowering the overpotentials, improving selectivity, and increasing the reaction kinetics of carbon dioxide conversion [101]. There are a lot of different catalysts reported in literature, although most of

them involve the use of metal complexes, such as salen ones [102,103], offering high values of TOF with orders of h^{-1} . On the other side, ionic liquids have been developed as a new catalyst, with a high dependence between TOF and the nature of the cation and anion which form the ionic liquid [104]. The order of TOF in these cases are in order of s^{-1} , allowing avoiding but the use of metals.

Scheme 2. General approach for CO_2 electrocatalytic system.

Up to now, the main disadvantage of electrochemical technologies is the use of organic solvents such as *N,N'*-dimethylformamide, which are well-known to be hazardous and flammable, as well as the use of large amount of supporting electrolyte [105]. For this reason, replacing organic aprotic solvents by ionic liquids (ILs), which are considered a greener option, would improve the process [106–109]. Ionic liquids are a family of solvents with unique properties that have led to their consideration as interesting alternatives, especially for electrochemical applications. Its wide electrochemical windows and good conductivities are obtained combining unsymmetrical bulky organic cations combined with hydrophobic anions [110–123]. For electrocarboxylation process, the use of ionic liquids offers the possibility of recycling the solvent as well as to improve the CO_2 capture due to their high solubility and conductivities [124–141].

Therefore, this work shows different strategies to valorize CO_2 using electrochemical technologies in ionic liquids. In one hand, with a series of nitro-compounds (Figure 1) using three different cathodes (carbon, copper and silver). On the other hand, the replacement of the nitro- group for a cyano- group, involves changes in the reaction mechanism and tune the CO_2 reduction products.

Figure 1. Structures of discussed compounds.

2. Materials and Methods

2.1. Materials

Carbueros Metálicos S.A. (Cornellà de Llobregat, Spain) provided the inert atmosphere gases (nitrogen, N_2 , or argon Ar) and carbon dioxide (CO_2) with purity of 99.9999%. All nitro- and cyano-compounds were obtained from Sigma-Aldrich (Madrid, Spain) and used without further purification. Anhydrous *N,N*-dimethylformamide (DMF) solvent (99.8%) was purchased from SDS (Madrid, Spain). The ionic liquid 1-methyl-1-ethylimidazolium bis(trifluoro-methanesulfonyl)imide (EMIM TFSI, purity 99%, $\text{H}_2\text{O} \leq 0.2\%$) was acquired from Solvionic (Toulouse, France) and was dried

under vacuum using activated molecular sieves for 24 h to make sure that the amount of water was always less than $\text{H}_2\text{O} \leq 0.001\%$ [142].

2.2. Methods

2.2.1. Cyclic Voltammetry

All electrochemical experiments were performed in an electrochemical conical cell with a set-up of the three-electrode system. For CV experiments, the working electrode is a vitreous carbon disk (1 mm diameter), silver disk (3 mm diameter) and copper disk (3 mm electrode). The counter electrode is a Pt disk (<1 mm diameter). All electrodes are polished using a 1 mm diamond paste. All the electrochemical potentials were measured using a saturated calomel electrode, SCE (+0.2411 V vs. SHE) isolated from the working electrode compartment by a salt bridge (salt-solution of the reference calomel electrode is separated from the electrochemical solution by a salt-bridge ended with a ceramic material frit, allowing ionic conduction between the two solutions and avoiding appreciable contamination). Ideally, the electrolyte solution present in the bridge is the same as the one used for the electrochemical solution in order to minimize junction potentials. When such a bridge is used, the ions in the bridge are present in large excess at the junction and they carry almost the whole of the current across the boundary. In our case were used DMF/0.1M TBA BF_4 (trying to weigh the same amount of support electrolyte that in the electrolyte solution) or EMIM TFSI, in both cases without electroactive substance. The error associated with the potential values is less than 5 mV. The ohmic drop can be one of the main sources of error when ILs are used as solvents, since they are more resistive media than aprotic polar solvents with 0.1 M concentration of supporting electrolyte. Before and after performing any electrochemical experiments, the solution is purged with inert gas (nitrogen or argon) for 20 min to avoid secondary reactions associated to OER and ORR due to dissolved oxygen in the solution [143,144].

The number of electrons involved in the first reduction process of nitro-compounds were determined by comparison with very well-known one-electron reduction of 9-fluorenone (redox probe), in the same medium using the same electrochemical set-up, by terms of cyclic voltammetry.

It is used 9-fluorenone and nitrobenzene as probe because both compounds have the same magnitude value of diffusion coefficient without further limitations (DMF ($10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$) nor ionic liquids ($10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$) [145,146]. The number of electrons involved in this first electron transfer was also confirmed by controlled-potential electrolysis.

2.2.2. Electrocarboxylation Processes

Cyano-compounds were electrolyzed at a negative potential of ~ 0.1 V more negative than the E_{pc} potential value under nitrogen/argon or carbon dioxide saturated solutions. When the reaction is completed, the resulting solution in the electrolysis is extracted with ether. The organic layer is dried with Na_2SO_4 and evaporated to yield a residue that is analyzed by gas chromatography-mass spectrometry, and Proton Nuclear Magnetic Resonance ($^1\text{H-NMR}$). Thus, all products obtained, and the commercial analogues were characterized by $^1\text{H-NMR}$. Measurements were made using a DPX360 (250 MHz) spectrometer (Bruker, Billerica, MA, USA) spectrometer. Proton chemical shifts were reported in ppm (d) (CDCl_3 , δ 7.26, or CD_3CN , δ 1.94). The J values are reported in Hz.

Benzonitrile (**8**). Colorless liquid, 31–35% yield. $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 7.70–7.55 (m, 3H), 7.47 (t, J = 7.4 Hz, 2H).

4-Cyanobenzoic acid (**9**). Yellow pale solid, 15–20% yield. $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 8.19 (d, J = 8.5 Hz, 2H), 7.78 (d, J = 7.6 Hz, 2H).

Benzoic acid (**10**). Colorless solid, 7–12% yield. $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 8.13 (d, J = 7.5 Hz, 2H), 7.62 (t, J = 6.8 Hz, 1H), 7.48 (t, J = 6.9 Hz, 2H).

When pure IL is used as electrolyte, the products of the electrolyzed solution are extracted with ether, allowing one to recover almost an 80% of the IL at the end of the experiment [147].

2.2.3. Determination of CO₂ Concentration

A thermal mass flowmeter of modular construction with a 'laboratory style' pc-board housing (EL-FLOW[®] Mass Flow Meter/Controller) from Bronkhorst Hi-Tec (Ruurlo, Netherlands), was used to monitor the CO₂ concentrations in the solution. Control valves were integrated to measure and control a gas flow from the lowest range of 0.2 up to 10 mL·min⁻¹.

3. Results and Discussion

3.1. Electrochemical Behaviour of Nitro-Compounds under Inert Atmosphere

The electrochemical behavior of a sequence of four *p*-nitro-compounds was studied in different solvents, and electrodes under inert atmosphere.

Cyclic voltammograms (CVs) of a 3–10 mL solution of **1–4** in DMF using 0.10 M of tetrabutylammonium tetrafluoroborate (TBA BF₄), and 1-methyl-1-ethylimidazolium bis(trifluoro-methanesulfonyl)imide (EMIM TFSI) were recorded at different scan rates (from 0.10 a 1.0 V s⁻¹) using glassy carbon (C, blue lines), Ag (black lines) and copper, Cu (red lines) as working electrodes under a N₂ atmosphere (Figure 2). Focusing in the first wave, the same general trend was observed in all electrodes and both solvents. Compounds **1–3** shows a monoelectronic fast reversible electron transfer, whereas compound **4** has an irreversible electron transfer (Table 1).

Figure 2. Cyclic voltammetry of 10 mM *p*-nitro compounds **1–4** with Ag (black line), Cu (red line) and C (blue line), under nitrogen atmosphere. Scan rate: 0.5 V·s⁻¹. Solution of DMF/0.1M TBA BF₄ (left) and solution of 3 mL EMIM TFSI (right).

Table 1. Standard potential (E^0), cathodic peak potential (in V vs. SCE, E_{pc}) and peak width (ΔE_p) for 1-4 in different solvents using different working electrodes (WE) at 20 °C.

DMF/0.1 M TBA BF ₄					
Entry	Nitro Derivative	WE	E _{pc} (V vs. SHE)	E ⁰ (V vs. SHE)	ΔE _p (mV)
1	1	Ag	−0.969	−0.919	72
2		Cu	−0.989	−0.889	70
3		C	−0.969	−0.899	70
4	2	Ag	−0.869	−0.839	60
5		Cu	−0.869	−0.839	72
6		C	−0.869	−0.839	60
7	3	Ag	−0.779	−0.699	67
8		Cu	−0.779	−0.689	68
9		C	−0.779	−0.689	67
10	4	Ag	−0.819	−0.719	83
11		Cu	−0.869	−0.699	90
12		C	−0.809	−0.769	70
EMIM TFSI					
Entry	Nitro Derivative	WE	E _{pc} (V vs. SHE)	E ⁰ (V vs. SHE)	ΔE _p (mV)
13	1	Ag	−0.949	−0.919	58
14		Cu	−0.949	−0.919	58
15		C	−0.959	−0.919	64
16	2	Ag	−0.889	−0.859	59
17		Cu	−0.899	−0.859	64
18		C	−0.889	−0.859	60
19	3	Ag	−0.859	−0.829	58
20		Cu	−0.859	−0.819	64
21		C	−0.859	−0.829	58
22	4	Ag	−0.889	−0.829	60
23		Cu	−0.919	−0.839	70
24		C	−0.929	−0.869	62

A closer look in CVs shows that of 4-iodonitrobenzene has irreversible wave at low scan rate, however it is possible to calculate the E^0 and the value of the kinetic constant associated to the chemical reaction ($k \sim 2 \cdot 10^4 \text{ s}^{-1}$) by increasing the scan rate (Scheme 3).

Scheme 3. Electron transfer followed by compounds 1-4.

The cyclic voltammogram of **4** also shows a second monoelectronic reversible wave following the first irreversible one. To check the nature of the product obtained after this first electron transfer, a control potential electrolysis of **4** was performed, being nitrobenzene (**5**) the only product obtained. Considering cyclic voltammetry and control potential electrolysis experiments under inert atmosphere, it is possible to conclude that 4-iodonitrobenzene follows an electron transfer mechanism (E) followed by a chemical reaction (C). Hence, in a first electrochemical step (E) the radical anion, **4**^{•−}, was generated, which evolves to cleavage C-I bond, obtaining nitrobenzene radical which produces nitrobenzene and iodine with an EC mechanism (Scheme 4).

Scheme 4. Proposal mechanism for 4-nitrobenzene electrochemical reduction under inert atmosphere.

3.2. Electrochemical Behaviour of Nitro-Compounds under CO₂ Atmosphere

Compounds **1-4** shows a clearly different behaviour when the cyclic voltammograms are recorded under CO₂ atmosphere, although they show the same general trend in aprotic solvent and ionic liquid. Also the follow same tendency in C, Ag and Cu working electrodes; there was a rising in current value of the reduction peak and its reversibility was lost (Figure 3), which indicates that p-nitrocompounds **1-4** follow a demeanor of an organic mediator for CO₂ indirect reduction through a homogeneous catalytic process (Scheme 5).

Figure 3. Cyclic voltammetry of 10 mM *p*-nitro compounds **1-4** with Ag (black line), Cu (red line) and C (blue line), under CO₂ atmosphere. Scan rate: 0.5 V·s⁻¹. Solution of DMF/0.1M TBA BF₄ (left) and solution of 3 mL EMIM TFSI (right).

Scheme 5. Proposal mechanism for general catalytic process between CO₂ and *p*-nitrobenzene halides.

In the case of carbon cathode, C, it is possible to see an oxidation peak in the corresponding anodic counter scan (copper and silver electrodes would be oxidized under this experimental conditions) between +0.19 and +0.44 V (vs. SHE). In all cases this peak corresponds to the oxidation of oxalate anion [148], which is formed after reducing the nitroaromatic compound. It is important to remark that the oxidation potential value obtained for oxalate is strongly dependent of the amount of water present in the solvent (Figure 4). The same results are obtained for a sample of pure tetrabutylammonium oxalate, since different amount of water are the oxalate oxidation peak shifts to higher oxidation potentials. Moreover, by using a carbon cathode it is possible to determine the concentration of oxalate formed upon reduction using CV, since the anodic peak current value is related with the oxalate concentration. Hence, we built a calibration curve using pure tetrabutylammonium oxalate for determining the amount of oxalate obtained upon reduction for each *p*-nitro compound. Finally, the TOF values were obtained using through FOWA's method. All the values were summarized in Table 2.

Figure 4. Cyclic voltammetry of 5 mM TBA₂C₂O₄ with glassy carbon under N₂ atmosphere. Scan rate: 0.5 V·s^{−1}.

Table 2. Catalytic parameters in homogeneous catalysis of CO₂.

Entry	Cat.	WE	E ⁰ _{catalyst} (V vs. SHE)		η (V)		TOF (s ⁻¹)		[C ₂ O ₄ ²⁻] (mM)	
			DMF/0.1M TBA BF ₄	EMIM TFSI	DMF/0.1M TBABF ₄	EMIM TFSI	DMF/0.1M TBA BF ₄	EMIM TFSI	DMF/0.1M TBA BF ₄	EMIM TFSI
1	1	Ag	−0.919	−0.919	0.90	0.92	7	6	-	-
2		Cu	−0.889	−0.919	0.88	0.92	24	11	-	-
3		C	−0.899	−0.919	0.90	0.91	9	6	18.2	3.41
4	2	Ag	−0.839	−0.859	1.00	0.98	10	7	-	-
5		Cu	−0.80	−0.859	1.00	0.97	8	13	-	-
6		C	−0.839	−0.859	1.00	0.98	10	5	33.4	6.57
7	3	Ag	−0.699	−0.829	1.09	1.01	29	7	-	-
8		Cu	−0.689	−0.819	1.09	1.01	22	5	-	-
9		C	−0.689	−0.829	1.09	1.01	17	6	38.1	9.37
10	4	Ag	−0.719	−0.829	1.05	0.98	8	7	-	-
11		Cu	−0.699	−0.839	1.00	0.95	14	6	-	-
12		C	−0.769	−0.869	1.06	0.94	17	5	3.56	1.12

Knowing that with carbon cathode it is possible to determine oxalate's peak with CV, with a calibration curve is determined the amount of oxalate obtained with each *p*-nitro compound. Also, it is possible to obtain TOF values through Fowa's method [92–96]. All the values were summarized in Table 2. Note that changing a methyl group by halides, the standard potential is lowered between 80–200 mV depending on electrode and halide. TOF values and oxalate amount obtained in DMF were higher than in EMIM TFSI. Faraday efficiencies were slightly higher in DMF solutions (from 30% to 88%) than in EMIM TFSI (from 10 to 51%) depending on the organic mediator used. These results can be explained due to low viscosity of the ionic liquid and coefficient diffusion value of CO₂ (Table 3).

Table 3. Viscosities and coefficient diffusion values of DMF and EMIM TFSI.

Entry	Solvent	Viscosity (mPa) ^a	Coefficient Diffusion (m ² /s) ^b
1	DMF	0.92	3.6 · 10 ^{−9}
2	EMIM TFSI	37.3	9.7 · 10 ^{−11}

^a Data obtained from Sigma Aldrich/Solvionic Safety Data Sheet (MSDS). ^b Data obtained from our laboratory research group [131].

Note, that it is possible to see an improvement in overpotential values with the use of ionic liquid instead DMF when *p*-nitrocompound has a halide group in its structure. Finally, note that it is possible to use small organic compound and ionic liquids to obtaining similar TOF values (in the order of s^{−1}) to previously published one for organometallic and more sophisticated organic compounds [89,138,149,150]. On the other hand, we observed that for compound 4 the anion radical generated after electron transfer evolves to nitrobenzene radical at the same time that the CO₂ reduction is electrocatalyzed. To check if it is possible to obtain electrocarboxylation product of 5 upon reaction of its radical with CO₂, a control potential electrolysis at −0.96 V (vs. SHE) was performed. After the passage of 1F, no electrocarboxylated aromatic compounds were formed, being oxalate the only electroreduced product of CO₂ formed. These results seem to indicate that the nitrobenzene radical formed upon reduction of 4 (Scheme 4) show a low nucleophilicity, being not able to attack and capture CO₂.

3.3. Electrocarboxylation of Cyano-Compounds 6 and 7 under CO₂ Atmosphere

According to previous results obtained in our research group [151], 4-iodobenzonitrile follows an ECE reduction mechanism in ionic liquids (Scheme 6). In the presence of CO₂ the electrogenerated anion intermediate leads to the corresponding carboxylation process. Hence, with the aim to obtain a stronger electrogenerated nucleophile, R[−] (Scheme 6), we decided to move from nitro to cyano

aromatic compounds. Thus, two new different *p*-cyanobenzene halides (4-chlorobenzonitrile (**6**) and 4-bromobenzonitrile (**7**)) were explored in this section.

Scheme 6. General overview for an ECE electrocarboxylation mechanism.

Figure 5 shows CVs at DMF/0.1M TBA BF₄ and one example in EMIM TFSI obtained under inert atmosphere and CO₂ atmosphere. All electrochemical parameters are summarized in Table 4. The same general trend was observed in aprotic solvents and ionic liquids. Moreover, not significant differences were detected when the nature of the working electrode was changed.

As it was expected compounds **6** and **7** exhibit an irreversible bielectronic wave under nitrogen atmosphere for any of the working electrodes investigated (Figure 5a,b). The same electrochemical behavior is observed when DMF is replaced by EMIM TFSI. A closer look to cyclic voltammograms reveals the electrocatalytic properties of silver as a working electrode, since the peak potential value of the reduction peak is shifted to less negative potentials. In order to determine the nature of the product formed upon reduction, a controlled potential electrolysis was performed. In all the cases benzonitrile, **8**, was the only product obtained after the passage of 2F. Taking into account CVs and the electrochemical data obtained from the electrolysis, it is possible to conclude that compound **6** and **7** follows an ECE mechanism. In a first electrochemical step, the radical anion of benzonitrile halide was generated. After that, a chemical reaction coupled to this first electron transfer led to a benzonitrile radical and the corresponding halide anion through a C-X cleavage reaction. Later, benzonitrile radical was reduced to its corresponding anion at the electrode surface (Scheme 7). It is important to remark that when cyano derivatives are used, it is possible to electrogenerate a strong nucleophile (benzonitrile anion), which is stable enough under our experimental conditions for reacting with CO₂ leading to the corresponding electrocarboxylated product.

Figure 5. Cyclic voltammetry of 10 mM *p*-cyano compounds **6** and **7** in DMF/0.1M TBA BF₄ with Ag (black line), Cu (red line) and C (blue line), under inert atmosphere (left) and CO₂ atmosphere (right). Scan rate: 0.5 V·s⁻¹.

Table 4. Electrochemical parameters for electroreduction of compounds **6** and **7** in DMF/0.1M TBA BF₄ and EMIM TFSI.

DMF/0.1M TBA BF ₄				
Entries	Cyano Derivative	WE	E _{pc} (V vs. SHE)	ΔE _p (mV)
1	6	Ag	−1.73	85
2		Cu	−1.80	78
3		C	−1.81	96
4	7	Ag	−1.47	201
5		Cu	−1.87	140
6		C	−1.73	99
EMIM TFSI				
7	6	Ag	−1.80	52
8		Cu	−1.80	65
9		C	−1.78	68
10	7	Ag	−1.61	70
11		Cu	−1.85	80
12		C	−1.71	72

Scheme 7. ECE proposal mechanism for the electrochemical reduction of **6** and **7**.

Figure 5c,d show that halobenzonitriles showed the same electrochemical behavior, a first two-electron reduction wave is observed for halobenzonitriles (Figure 5a,b) in nitrogen and carbon dioxide atmosphere. In none of the cases the presence of oxalate anion was detected.

Once the electrochemical reduction mechanism of halobenzonitriles under CO₂ atmosphere was disclosed, electrocarboxylation process were performed using carbon graphite rod. For all the compounds the applied potential was 0.1 V more negative than potential of the first reduction wave. The results of carboxylation reactions were summarized in Table 5. It could observe that *p*-cyanobenzoic acid (**9**) and benzoic acid (**10**) were obtained in moderated yields after the passage of 2F. Benzonitrile (**8**) is also obtained, showing that there was a competition between carboxylation and protonation process.

Benzoic acid obtention would be explained because at the potential of electrolysis, *p*-cyanobenzoic acid is also reduced, since its reduction potential is c. a. -1.36 V (vs. SHE).

Table 5. Results of the electrocarboxylation of **6** and **7** at 2F.

Entries	Reagent	Cathode	Solvent	Electrochemical Conditions	% Yield (Conversion Rate)			Reagent
					Carboxylated Products		Ar-H	
				E_{ap} (V vs. SHE)	9	10	8	
1	6	C	DMF	-1.86	20 (32%)	10 (32%)	32	38
2			EMIM TFSI	-1.86	15 (26%)	7 (26%)	35	43
3	7	C	DMF	-1.81	18 (28%)	12 (28%)	34	36
4			EMIM TFSI	-1.81	16 (28%)	10 (28%)	31	43

Electrocatalytic Behaviour of Cyano-Compounds **6** and **7** under CO_2 Atmosphere

Figure 6 shows several cyclic voltammograms of **6** and **7** under nitrogen and CO_2 atmosphere using silver and glassy carbon (GC) as a cathode. The use of DMF as a solvent and GC as a cathode allows to see a second monoelectronic fast reversible wave after first one (Figure 5). This second wave corresponds to the electrochemical reduction of benzonitrile, which is the only product obtained after the reduction of compounds **6** and **7**. It is noticeable that benzonitrile acts as a redox mediator for CO_2 reduction when reaction is performed under CO_2 atmosphere, since there is an increase of the peak current value and a loss of reversibility of this second reduction wave (homogeneous indirect CO_2 reduction catalytic process (Figure 6a,c)).

Figure 6. Cyclic voltammograms in DMF/0.1M under nitrogen atmosphere and 20–60 mM $[\text{CO}_2]$ atmosphere using a solution of 10 mM of **6** (a) with GC (b) Ag. A solution of 10 mM of **7** with (c) GC and (d) Ag. Scan rate 0.5 V s^{-1} .

The use of silver electrode allows to tune the CO_2 reduction mechanism. In this case the current value of the first reduction is increasing as well as the peak potential value is shifting when the

concentration of CO₂ is rising. These results can be explained taking into account that under these experimental conditions two electrochemical processes are happening at the electrode surface at same potential; the reduction of the cyanoaromatic halide and the direct reduction of CO₂ (Figure 6b,d). The same trend is observed with the use of copper cathode and a ionic liquid with wide electrochemical window, such as 1-methyl-1-propylpiperidinium bis(trifluoromethylsulphonyl)-imide ([PP13] TFSI). Note that in this cases EMIM TFSI cannot be used as a IL, since the reduction of the EMIM cation takes place c.a. −2.06 V vs. SHE. [151].

4. Conclusions

In conclusion, we describe an efficient approach for producing high value products using CO₂ as building blocks. The methodology employed is based on electrochemical techniques and ILs, which provide eco-friendly chemistry solutions. These can be employed to offer a potential long-term strategy for using CO₂ feedstocks. There are two different strategies to obtain a CO₂ valorization product depending on the functional group, nitro or cyano, of the aromatic halide. An electrocatalytic process using a homogeneous catalysis, which provides an easy way of obtaining oxalate is seen when nitro derivatives are used, removing metal complexes as a catalyst. The use of cyano derivatives allows to tune the reactivity in function of the reduction potential value applied from electrocarboxylated products (via a nucleophile-electrophile reaction) to oxalate. These electrochemical reactions were performed with three different electrodes and in aprotic solvents and ionic liquids, which all showed the same trend. This opens the possibility of using a copper electrode and ionic liquids to valorize CO₂, which would be a cheaper and greener alternative.

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