Article

Electrocatalytic Processes for the Valorization of CO₂: Synthesis of Cyanobenzoic Acid Using Eco-Friendly Strategies

Silvia Mena[ID]**, Iluminada Gallardo**[ID] **and Gonzalo Guirado** *[ID]

Departament de Química, Universitat Autònoma de Barcelona, Campus UAB, 08193 Bellaterra, Barcelona, Spain; silvia.mena@uab.cat (S.M.); iluminada.gallardo@uab.cat (I.G.)
* Correspondence: gonzalo.guirado@uab.cat; Tel.: +34-93-581-4882

check for updates

Abstract: Carbon dioxide (CO_2) is a known greenhouse gas, and is the most important contributor to global warming. Therefore, one of the main challenges is to either eliminate or reuse it through the synthesis of value-added products, such as carboxylated derivatives. One of the most promising approaches for activating, capturing, and valorizing CO_2 is the use of electrochemical techniques. In the current manuscript, we described an electrocarboxylation route for synthesizing 4-cyanobenzoic acid by valorizing CO_2 through the synergistic use of electrochemical techniques ("green technology") and ionic liquids (ILs) ("green solvents")—two of the major entries in the general green chemistry tool kit. Moreover, the use of silver cathodes and ILs enabled the electrochemical potential applied to be reduced by more than 0.4 V. The "green" synthesis of those derivatives would provide a suitable environmentally friendly process for the design of plasticizers based on phthalate derivatives.

Keywords: ionic liquids; carbon dioxide; electrochemistry; green chemistry; cyanobenzoic acid

1. Introduction

Fossil fuels in the form of coal, oil, and natural gas account for 80% of the world's energy use and have caused increases in the Greenhouse Gas (GHG) concentrations of the atmosphere. These have led to global warming, climate change, and ozone layer depletion, with destructive impacts on human society and the economy. In the last four decades, despite global attempts to mitigate emissions, the world saw more than 100% growth in annual CO_2 emissions, which surpassed 32 billion tons in 2011. These global CO_2 emissions will continue to increase and are projected to reach 36 billion tons in 2020, and double that by 2050 if appropriate climate change mitigation measures are not put in place [1–3]. In this sense, different research strategies are currently being developed for the activating, capturing, and valorizing of CO_2. Hence, CO_2 uses are generally classified into different categories, such as direct use and/or conversion to chemicals and energy [4–11].

Carboxylic acids and esters are important classes of chemicals that are widely found in pharmaceuticals, polymers, agrochemicals, natural products, and biological systems, and they have been widely applied as versatile building blocks in organic synthesis [12–14]. For instance, the utilization of CO_2 as a C1 synthon for incorporation with lithium phenolate, or Grignard reagents for the synthesis of carboxylic acids have been well known for more than a century. On the other hand, metal-catalyzed direct insertion of CO_2 into different compounds is another valuable method for the preparation of carboxylic acids with high selectivity. This approach is widely used to obtain carboxylic analogues from carbon–halide, carbon–boron, carbon–oxygen, aromatic and alkyl reagents, etc. [15–22]. Moreover, the development of new methods that take advantage of the abundant and inexpensive CO_2 without catalysts (carbon monoxide, phenols, and others), for the transformation of aryl halides into their corresponding aryl carboxylic acid provides an attractive option for their assembly [23,24].

In this sense, the CO_2 valorization by electrochemical routes is receiving increasing attention as a way to obtain chemicals with added value, and as a promising option to chemically store renewable energy from intermittent sources like solar or wind, thus reducing our reliance on fossil fuels. Although the benefits of using electrochemical approaches to perform classic chemical reactions in the design of greener and more suitable processes are well established, the main drawbacks of performing electrochemical reactions are the use of non-volatile organic polar compounds, which are well-known hazardous substances, as well as the use of supporting electrolytes in high concentration [25–29]. In this sense, the replacement of electrolytes based on an organic solvent with ionic liquids (ILs), which are considered "green solvents" would solve this problem. Ionic liquids (ILs) are a family of solvents with unique properties that have led to their consideration as interesting alternatives and more effective solvents in many applications, including electrochemistry [30–32] and CO_2 storage and capture [33–35].

Therefore, the growing interest in the electrochemical valorization of CO_2 has resulted in different innovative attempts, including the use of ILs, in order to improve the performance of these electrochemical approaches.

In the present work, a description is presented of an electrocarboxylation route for synthesizing 4-cyanobenzoic acid by valorizing CO_2 through the synergistic use of electrochemical techniques and ILs (two of the major entries in the general green chemistry tool kit). The "green" synthesis of 4-cyanobenzoic acid is produced through the electrochemical cleavage of a carbon-iodide bond and the subsequent capture of CO_2 (Scheme 1). It was decided to perform the electrocarboxylation process from 4-iodobenzonitrile, since less energy is required to break it down than the C–F bond, the C–Cl bond, and even the C–Br bond. Moreover, electrocatalytic effects related to the nature of the cathodes and the use of ILs will also be investigated for reducing the electrochemical potential needed. The optimization of electrocarboxylation conditions would open a suitable environmentally friendly process for obtaining 4-cyanobenzoic derivatives, which can be potentially useful for the designing of "green" plasticizers based on phthalate derivatives [12].
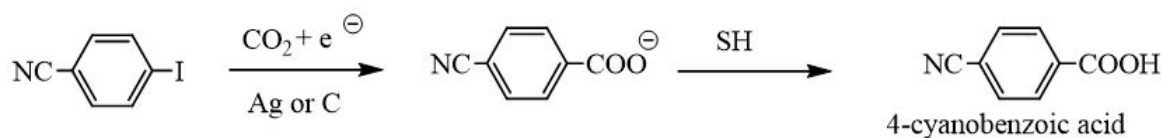
Scheme 1. Electrocarboxylation of 4-iodobenzonitrile.

2. Results and Discussion

To establish the optimal experimental conditions for the optimal electrochemical capture of CO_2, the electrochemical behavior of 4-iodobenzonitrile (**1**) was studied in different solvents and electrodes under an inert atmosphere.

2.1. Electrochemical Reduction of 4-Iodobenzonitrile under an Inert Atmosphere

Electrochemical Reduction Mechanism of 4-Iodobenzonitrile on Carbon and Silver Cathodes

Cyclic voltammograms (CVs) of a 10 mL solution of **1** in dimethylformamide (DMF) using 0.10 M of tetrabutylammonium tetrafluoroborate (TBA BF_4) were recorded at different scan rates (from 0.10 a 1.0 V s^{-1}) using glassy carbon (GC, dotted line) and Ag (solid lines) as working electrodes under a N_2 atmosphere, and are depicted in Figure 1. The same general trend was observed in both cases, a first two-electron irreversible wave followed by a second reversible one-electron wave. This second electron transfer corresponded to the electrochemical reduction of benzonitrile, which is in agreement with previous studies reported in the literature under similar experimental conditions [36]. A closer look at the CVs revealed that the reduction potential value of **1** was reduced by at least 0.46 V (from −1.83 V to −1.37 V), when Ag was used as cathode material instead of GC. The reduction of the

over-potential showed a well-defined electrochemical signal (Figure 1). Hence, the use of silver as a cathode introduced electrocatalytic properties for the current reduction processes performed in an aprotic organic electrolyte, such as DMF + 0.10 M TBA BF$_4$.
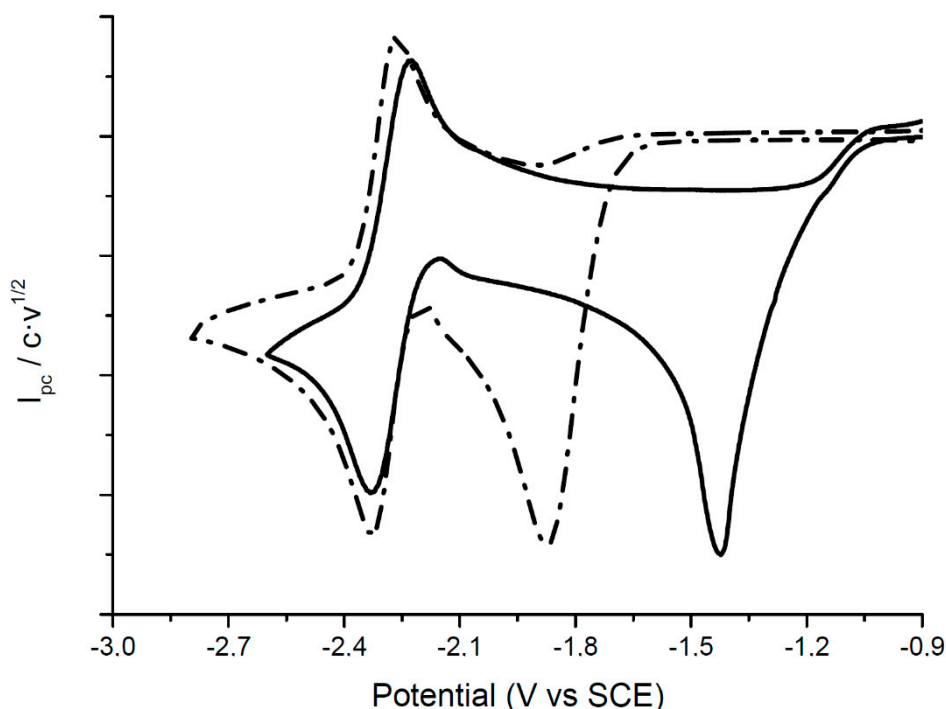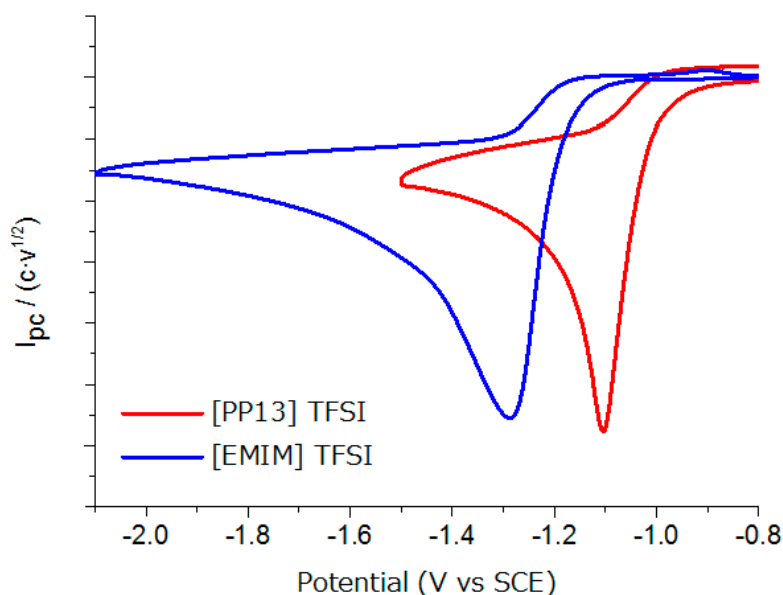

Figure 1. Cyclic voltammograms of a 5 mL DMF/0.10 M TBABF$_4$ solution containing 10 mM 4-iodobenzonitrile using silver, Ag, (solid line) and glassy carbon, GC, (dotted lines) under a nitrogen atmosphere. Scan rate 0.5 V s^{-1}.

The same electrocatalytic effect was observed when DMF was replaced by ionic liquids (ILs). Thus, when 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM]TFSI) and 1-methyl-1-propylpiperidinium bis(trifluoromethylsulphonyl)-imide ([PP13]TFSI) were used as electrolytes, the reduction potential value of **1** was reduced by approximately (ca.) 0.5 V (Figure 2). Note that ILs can also act as a co-catalyst when silver is used as a working electrode, since the reduction potential value of **1** is ca. 0.1 V lower compared to DMF + 0.10 M TBABF$_4$ (Table 1). Hence, the solvation process of 1 $^-$ appeared to be more effective in the case of using a high concentration of cations (ILs) than tetrabutylammonium salts at low concentrations (0.1 M TBABF4 in DMF). Besides, it seemed that the presence of pyrrolidinium cations in the IL composition led to stronger coulombic interactions, which rendered better solvation of 1$^-$.

Table 1 summarizes the electrochemical data obtained for the electrochemical reduction of **1** using several solvents and cathode materials. In all the cases a fast, irreversible, two-electron reduction wave was observed, whereas the electron transfer seemed to be faster in silver than in glassy carbon, since the peak width value was reduced from ca. 100 mV (slow electron transfer) to ca. 60 mV (fast electron transfer) [37–40].

To fully establish the electrochemical reduction mechanism of **1** in ionic liquids, a controlled potential electrolysis after the first reduction wave (at a potential value of ca. 0.1 V more negative than the E$_{pc}$) was performed under an inert atmosphere using either carbon graphite or silver cathodes. The analysis of the sample after the electrolysis showed that, in all the cases, benzonitrile, **2**, was the only product formed after the passage of 2F (C mol^{-1}) (Figure 3). The electrochemical processes were monitored by cyclic voltammetry.
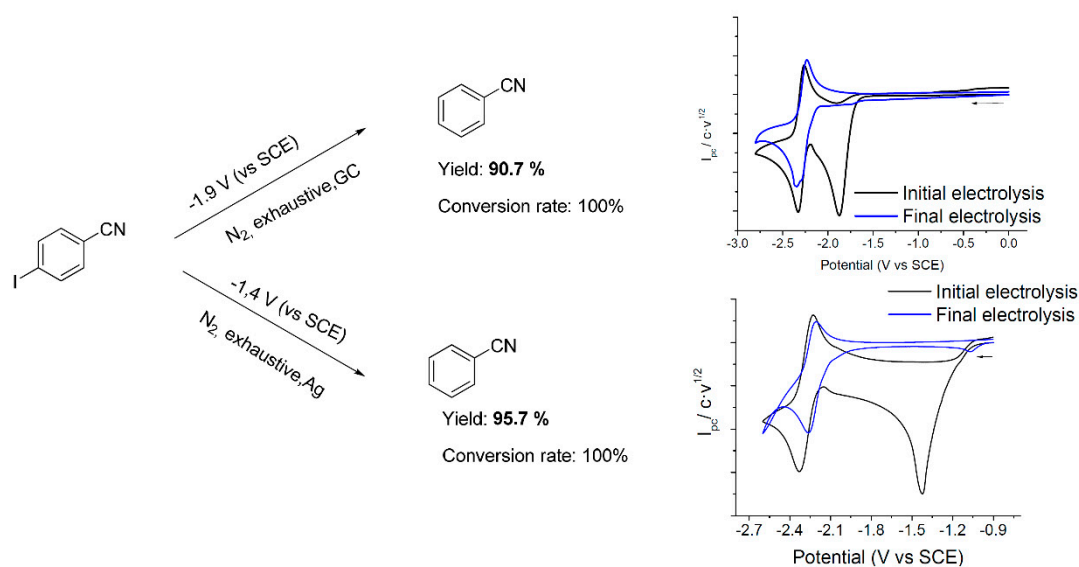
Figure 2. Cyclic voltammograms of a 5 mL solution, [PP13]TFSI (red line) and [EMIM]TFSI (blue line), containing 10 mM 4-iodobenzonitrile using Ag under a nitrogen atmosphere. Scan rate 0.5 V s^{-1}.

**Table 1.** Electrochemical parameters for the electrochemical reduction of **1**.

Solvent	Number of Electrons [1]	Glassy Carbon Cathode		Silver Cathode		Electrocatalytic Effect (kcal mol^{-1}) [3]
		E_{pc} (V)	ΔE_{pc} (V) [2]	E_{pc} (V)	ΔE_{pc} (V)[b]	
DMF [4]	2	−1.85	0.09	−1.37	0.06	10.4
[PP13]TFSI	2	−1.83	0.12	−1.07	0.07	17.5
[EMIM]TFSI	2	−1.84	0.08	−1.29	0.06	12.7

[1] Number of electrons involved in the first electron transfer determined by comparison with a 9-Fluorerone redox probe. [2] $\Delta E_p = E_{pc} - E_{pc/2}$. [3] Electrocatalytic effect: E_{pc}(GC) − E_{pc}(Ag). [4] DMF contains 0.10 M TBABF$_4$.

Figure 3. Experimental conditions and the cyclic voltammogram of a 5 mL solution of **1** (10 mM) before (black line) and after (blue line) controlled potential electrolysis under an inert atmosphere with a glassy carbon electrode (top) and silver electrode (bottom). Scan rate: 0.5 V s$^{-1.}$

Taking into account the cyclic voltammetry and controlled potential electrolysis experiments, it is possible to conclude that **1** followed the Electron transfer, Chemical reaction, Electron transfer (ECE) mechanism. Hence, in a first electrochemical step (E) the radical anion, **1⁻**, was generated. A chemical reaction (C) coupled to this first electron transfer led to a benzonitrile radical and an iodide anion through a C–I bond cleavage reaction. Finally, the radical was reduced to an anion at the electrode surface (E), which later protonated by reacting with the solvent (Scheme 2). Note that the electrochemical generation of benzonitrile anion, which acts as a nucleophile leading to benzonitrile, opened the door to incorporate CO_2 via nucleophile-electrophile reaction through the electrochemical reduction of **1**.
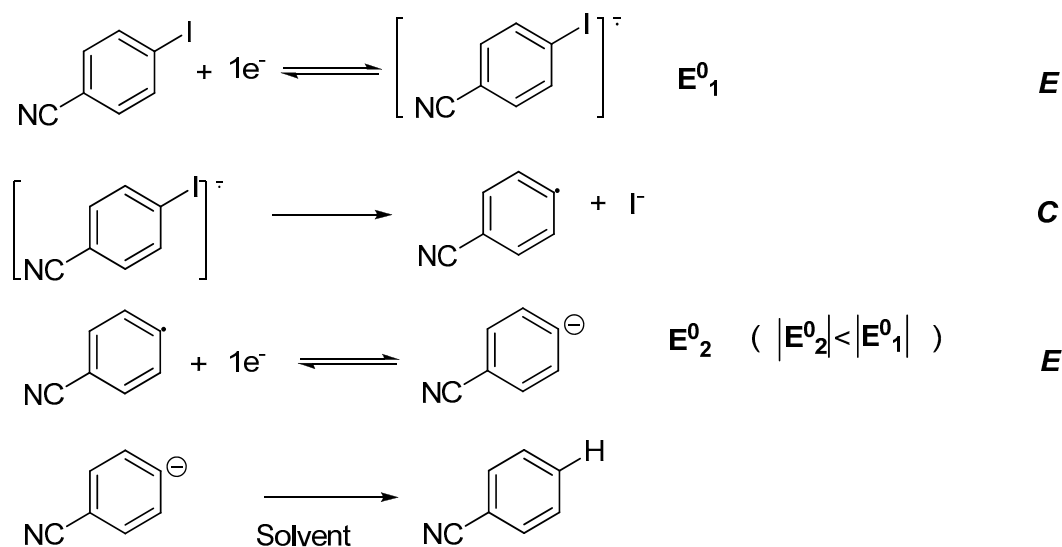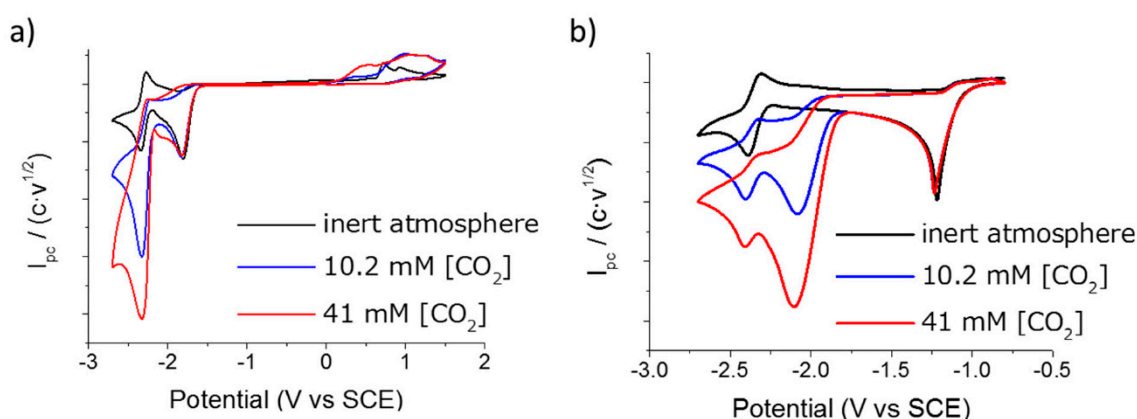
Scheme 2. ECE mechanism proposal for the electrochemical reduction of **1** for both media.
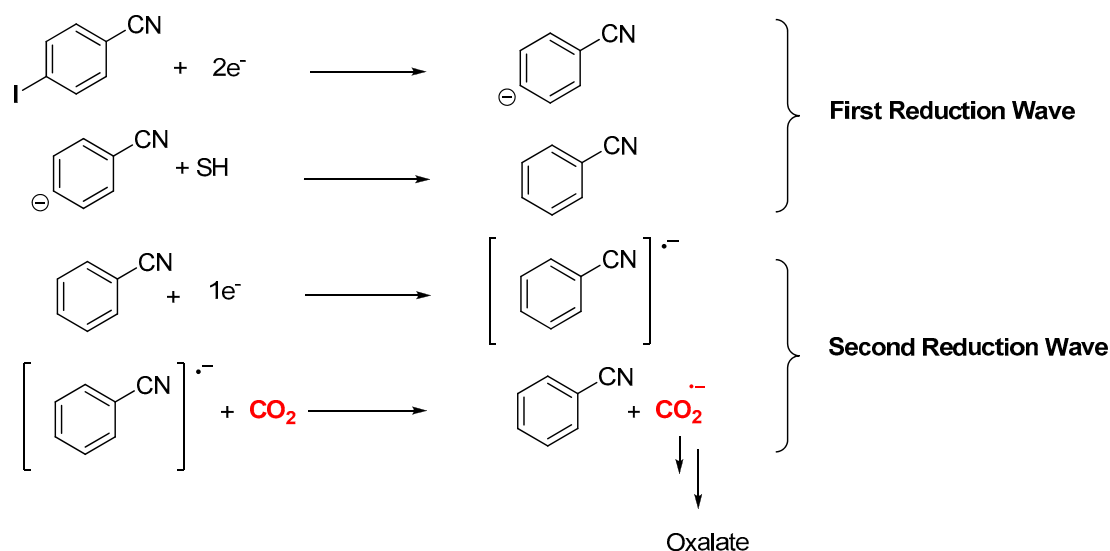
2.2. Electrochemical Reduction of 4-Iodobenzonitrile under a Carbon Dioxide (CO_2) Atmosphere

Electrochemical Reduction Mechanism of 4-Iodobenzonitrile on Carbon and Silver Cathodes

4-Iodobenzonitrile (**1**) showed a different electrochemical behavior at GC and silver cathodes in DMF under a CO_2 atmosphere. When GC was used, two reduction peaks were observed at −1.83 V and −2.35 V, the first one corresponding to the electrochemical reduction of **1**, and the second one to the electrochemical reduction of benzonitrile (Figure 4a). It is worth noting that in the presence of CO_2 there was an increase in the peak current value of this second reduction peak and a loss of reversibility, which indicated that the benzonitrile was acting as an organic mediator for the reduction of CO_2 through a homogeneous indirect catalytic process [41,42]. In the corresponding anodic counter scan, a new oxidation peak was observed at 0.45 V, which corresponded to the oxidation of the oxalate anion generated in the CO_2 reduction process under a saturated CO_2 atmosphere [43] (Scheme 3). Note that the peaks at higher oxidation potential values corresponded to the oxidation of iodide and triiodide, respectively. Due to the low oxidation potential value of silver, it was not possible to record any anodic counter scan so as to detect the nature of the anionic products formed.

Figure 4. Cyclic voltammograms of 5 mL solution in DMF/0.10 M TBABF$_4$ containing 10.2 mM 4-iodobenzonitrile under a nitrogen atmosphere and CO_2 atmosphere using (**a**) GC and (**b**) Ag. Scan rate 0.5 V s^{-1}.

Scheme 3. Mechanism proposal for the electrochemical reduction of **1** using a GC electrode under a CO_2 atmosphere.

The CV of **1** at the silver cathode under a CO_2 atmosphere in DMF showed three reduction peaks at −2.23 V, −2.09, and −2.40 V vs. SCE. The first and third peaks corresponded to the electrochemical reduction of **1** and benzonitrile, respectively. The second peak corresponded to the electrochemical reduction of CO_2. This assignment of the second reduction peak to the electrochemical reduction of CO_2 can be confirmed since the peak current value was directly linked to the CO_2 concentration, as it can be seen in Figure 4b. In the case of using silver as a working electrode, the electrochemical processes and their associated reactivity were easily controlled by the applied potential. Note that in this case, since the electrochemical reduction of CO_2 occurred prior to the benzonitrile reduction, no electrocatalytic processes were observed related to the role of benzonitrile as a redox mediator (Scheme 4).

The same general electrochemical trend was observed when DMF was replaced by [PP13]TFSI under a N_2 and a CO_2 atmosphere at the GC and silver electrodes. However, when using [EMIM]TFSI, the electrochemical reduction of benzonitrile was not detected in any of the cases due to the fact that the reduction of the imidazolium cation appeared at less negative potentials either in inert or CO_2 atmospheres [44].
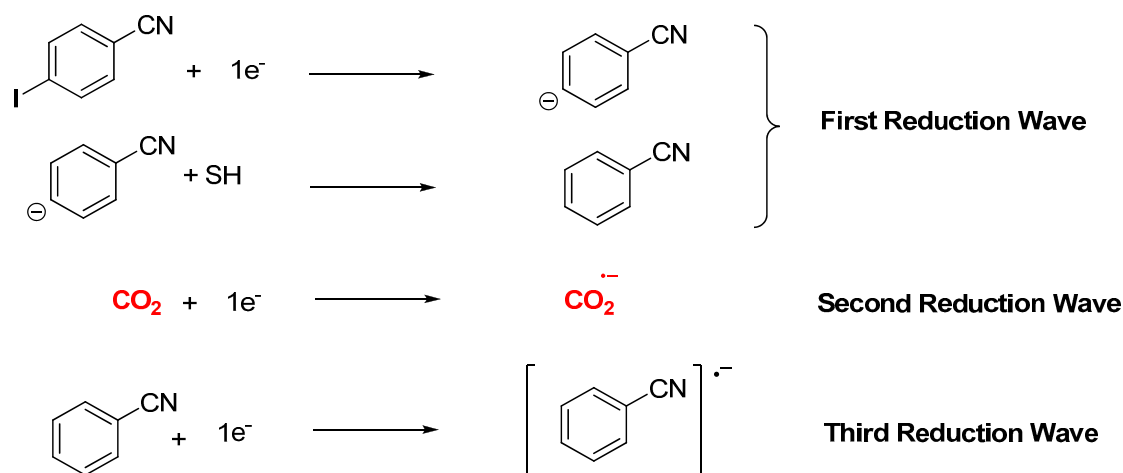
Scheme 4. Mechanism proposal for the electrochemical reduction of **1** using an Ag electrode under a CO_2 atmosphere.

### 2.3. Electrochemicarboxylation of 4-Iodobenzonitrile

Once the electrochemical reduction mechanism was disclosed, electrocarboxylation processes were performed using a carbon graphite rod and a silver foil electrode after its first reduction wave (ca. −1.9 V) under a CO_2 atmosphere. The results are summarized in Table 2. It is important to note that, when silver was used as a cathode, the electrochemical potential required was 0.5 V lower. A closer look at the data when carbon electrode was used indicates that when the electrocarboxylation process was performed in [EMIM]TFSI, there was a loss of efficiency and no electrocarboxylation products were obtained (entry 1). Those facts can be easily explained by taking into account the IL electrochemical window and the acidity of the C_2–H of the imidazolium moiety. The replacement of the carbon cathode for silver allowed the efficiency of the electrosynthesis to increase, since the reduction potential applied was less negative, although no electrocarboxylated product was observed, again due to the acidity of the IL cation (entry 4).

Table 2. Results of the electrocarboxylation of **1**.

|			Electrochemical Conditions		Yield		
					Electrocarboxylated Products (Conversion Rate)		Ar-H
Entries	Solvent	Cathode	$E_{applied}$ (V)	F (C mol^{-1})	3	4	2
1	[EMIM]TFSI	Carbon	−1.9	3.3	-	-	45%
2	[PP13]TFSI	Carbon	−1.9	2.0	8% (19%)	2% (19%)	33%
3	[PP13]TFSI	Carbon	−1.9	3.0	-	12% (21%)	44%
4	[EMIM]TFSI	Silver	−1.4	1.5	-	-	95%
5	[PP13]TFSI	Silver	−1.4	1.0	5% (10%)	-	45%
6	[PP13]TFSI	Silver	−1.4	2.5	26% (29%)	-	66%
7	[PP13]TFSI	Silver	−1.4	3.0	30% (30%)		70%
8	[BMPyr]TFSI	Silver	−1.4	1.0	10% (33%)		20%
9	[N1114]TFSI	Silver	−1.4	2.4	29% (38%)		48%

The use of an IL composed of non-acidic cations enabled electrocarboxylated products to be obtained. When [PP13]TFSI was used, around 10% of electrocarboxylated products (p-cyanobenzoic acid (**3**) and benzoic acid (**4**)) were obtained using carbon electrodes (Scheme 5, entries 2 and 3). The use of a high reduction potential value caused the appearance of an unexpected carboxylation product, **4**, which should be related to the further electrochemical reactions of compound **3** that take place under these electrochemical conditions. Note that when the charge passed to the system increased, the only

product obtained was **4** in a 12% yield (entry 3). To confirm this hypothesis, a controlled potential electrolysis of **3** was performed under the same electrochemical and chemical conditions previously described in entry 3, revealing the formation of benzoic acid in a ca. 25% yield.
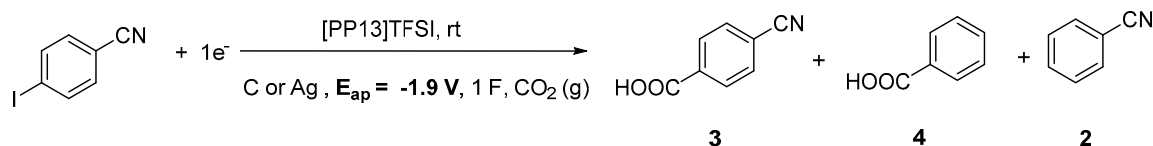
Scheme 5. Electrocarboxylation of **1** acid under CO_2 atmosphere using graphite as a cathode.

The use of silver cathodes allowed working under milder conditions, and as a consequence, not only were the electrocarboxylation yields almost three times higher, but also the selectivity of the increases, and only **3** was obtained as a carboxylation product in [PP13]TFSI (entries 5–7). Only compounds **2** and **3** were obtained in 70% and 30% yields, respectively, when exhaustive controlled potential electrolysis was performed. These results can also be reproduced using two different ILs consisting of non-acidic cations, such as 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulphonyl)imide ([BMPyr]TFSI) and *N*-trimethyl-*N*-butylammonium methylimidazolium bis(trifluoromethylsulphonyl)imide ([N1114]TFSI), entries 8 and 9 respectively. In all the cases, conversion rates ca. 30% were obtained (Scheme 6).
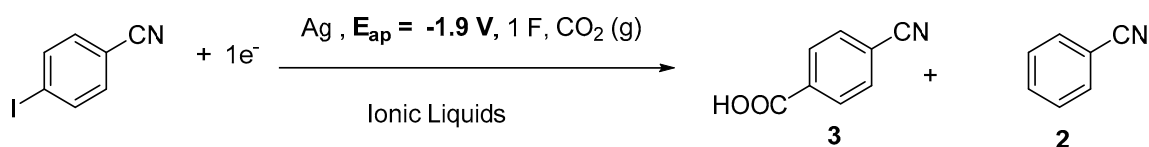
Scheme 6. Electrocarboxylation of **1** under CO_2 atmosphere using silver as a cathode.

3. Materials and Methods

3.1. Materials

Carbon dioxide (CO_2) and nitrogen (N_2) were purchased from Carburos Metálicos S.A. (Cornellà de Llobregat, Spain), purity of 99.9999%). All of the commercially available reagents, p-cyanobenzoic acid, 4-iodobenzonitrile, benzonitrile, *N,N*-dimethylformamide (DMF) and tetrabutylammonium tetrafluoroborate ($TBABF_4$) were acquired from Sigma-Aldrich (Madrid, Spain) with maximum purity and used as received. 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM]TFSI), 1-methyl-1-propylpiperidinium bis(trifluoromethylsulphonyl)imide ([PP13]TFSI), 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulphonyl)imide ([BMPyr]TFSI) and *N*-trimethyl-*N*-butylammonium methylimidazolium bis(trifluoromethylsulphonyl)imide ([N1114]TFSI) were acquired from Solvionic (Toulouse, France)and were dried with activated molecular sieves for 24 h in order to guarantee that the amount of water was always less than 100 ppm.

3.2. Electrochemical Experiments

An electrochemical conical cell was used for the set-up of the three-electrode system. For cyclic voltammetry (CV) experiments, the working electrode was a silver disk with a diameter of 1.6 mm and a glassy carbon disk with a diameter of 1 mm. It was polished using a 1 mm diamond paste. The counter electrode was a Pt disk <1 mm in diameter. All of the potentials were reported versus an aqueous saturated calomel electrode (SCE) isolated from the working electrode compartment by a salt bridge. The salt solution of the reference calomel electrode was separated from the electrochemical solution by a salt bridge ended with a frit, which was made of a ceramic material, 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. The error associated with the potential values was 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 polar aprotic solvents with 0.10 M concentration of supporting electrolytes.

Due to the low conductivity and larger viscosity of RTILs (Room Temperature Ionic Liquids), in order to facilitate the direct comparison between the cyclic voltammograms in the different media, the current values obtained were first normalized by the concentration and the scan rate ($Ip/cv^{1/2}$). Later, those values were also normalized and the relationship between the four solvents can be expressed by a total normalization coefficient. This coefficient can be expressed as a ratio between DMF/[EMIM]TFSI, DMF/[PP13]TFSI, DMF/[N1114]TFSI, and DMF/[BMPyr]TFSI 3.0, 1.7, 6.0, and 2.7, respectively.

For electrolysis experiments, the disc working electrodes were replaced by a graphite carbon bar and a silver foil. The counter (Pt bar) and reference (SCE) electrodes were separated from the electrochemical solution by a salt bridge filled by the electrolyte solution. The salt bridge ended with a frit, which was made of a ceramic material, avoiding appreciable contamination. Compounds were electrolyzed at a negative potential of 0.10 V more negative than the E_{pc} potential value under nitrogen- or carbon-saturated solutions. When the reaction was completed, the mixture was extracted into water/ether mixtures. The organic layer was dried with Na_2SO_4 and evaporated to yield a residue. All products obtained were characterized by Proton Nuclear Magnetic Resonance (^{1}H-NMR) and Gas Chromatography (GC) by comparison with their respective pure commercially available analogues.

3.3. Determination of the CO_2 Concentration in ILs

A thermal mass flow meter of modular construction with a 'laboratory style' pc-board housing (EL-FLOW® Mass Flow Meter/Controller, Bronkhorst Hi-Tec, Ruurlo, Netherlands) was used to monitor the CO_2 concentrations in the solution [28]. Control valves are integrated to measure and control a gas flow from the lowest range of 0.2–10 mL/min.

4. Conclusions

This manuscript describes a new "environmentally-friendly" electrochemical approach for producing highly valuable compounds using CO_2 as a building block in ILs. The selection of the solvent and the nature of the cathode material are crucial, since it helps to overcome the main drawbacks associated with previous processes reported in the literature, in which organic solvents, redox mediators and large quantities of supporting electrolytes are employed. The use of silver instead of carbon cathodes enables p-cyanobenzoic acid to be obtained from the electrochemical reduction of 4-iodobenzonitrile under mild experimental conditions with moderate yields and conversion rates under a CO_2 atmosphere. The use of non-acidic ILs also makes the electrocarboxylation process more environmentally friendly, since it is not only able to avoid the use of organic solvents and large quantities of supporting electrolytes, but also the solvation process of 1^- appears to be more effective. Hence, the use of ILs (high concentration of cations) instead of tetrabutylammonium salts at low concentrations (0.1 M TBABF4 in DMF) enables the electrochemical potential applied to be also reduced. This study opens the door to develop new strategies for the synthesis of similar derivatives, such as phthalates, by following this "greener" route.

Author Contributions: G.G. conceived and designed the experiments; S.M. performed the experiments and analyzed the data. G.G. and I.G. wrote the paper and approved the final version for its publication.

Conflicts of Interest: The authors declare no conflict of interests.

References

1. Veríssimo, D.; Macmillan, D.C.; Smith, R.J.; Crees, J.; Davies, Z.G. Has Climate Change Taken Prominence over Biodiversity Conservation? *Bioscience* **2014**, *64*, 625–629. [CrossRef]

2. Oertel, C.; Matschullat, J.; Zurba, K.; Zimmermann, F.; Erasmi, S. Greenhouse Gas Emissions from Soils—A Review. *Chemie der Erde-Geochemistry* **2016**, *76*, 327–352. [CrossRef]

3. Nejat, P.; Jomehzadeh, F.; Taheri, M.M.; Gohari, M.; Muhd, M.Z. A Global Review of Energy Consumption, CO_2 emissions and Policy in the Residential Sector (with an Overview of the Top Ten CO_2 Emitting Countries). *Renew. Sustain. Energy Rev.* **2015**, *43*, 843–862. [CrossRef]

4. Albo, J.; Alvarez-Guerra, M.; Castaño, P.; Irabien, A. Towards the Electrochemical Conversion of Carbon Dioxide into Methanol. *Green Chem.* **2015**, *17*, 2304–2324. [CrossRef]

5. Brunel, P.; Monot, J.; Kefalidis, C.E.; Maron, L.; Martin-Vaca, B.; Bourissou, D. Valorization of CO_2: Preparation of 2-Oxazolidinones by Metal-Ligand Cooperative Catalysis with SCS Indenediide Pd Complexes. *ACS Catal.* **2017**, *7*, 2652–2660. [CrossRef]

6. Bobbink, F.D.; Van Muyden, A.P.; Gopakumar, A.; Fei, Z.; Dyson, P.J. Synthesis of Cross-Linked Ionic Poly(Styrenes) and Their Application as Catalysts for the Synthesis of Carbonates from CO_2 and Epoxides. *Chempluschem* **2017**, *82*, 144–151. [CrossRef]

7. Cheah, W.Y.; Ling, T.C.; Juan, J.C.; Lee, D.J.; Chang, J.S.; Show, P.L. Biorefineries of Carbon Dioxide: From Carbon Capture and Storage (CCS) to Bioenergies Production. *Bioresour. Technol.* **2016**, *215*, 346–356. [CrossRef]

8. Huang, C.H.; Tan, C.S. A Review: CO_2 Utilization. *Aerosol Air Qual. Res.* **2014**, *14*, 480–499. [CrossRef]

9. Kurlov, A.; Broda, M.; Hosseini, D.; Mitchell, S.J.; Pérez-Ramírez, J.; Müller, C.R. Mechanochemically Activated, Calcium Oxide-Based, Magnesium Oxide-Stabilized Carbon Dioxide Sorbents. *ChemSusChem* **2016**, *9*, 2380–2390. [CrossRef]

10. Pan, S.Y.; Chiang, P.C.; Pan, W.; Kim, H. Advances in State-of-Art Valorization Technologies for Captured CO_2 toward Sustainable Carbon Cycle. *Crit. Rev. Environ. Sci. Technol.* **2018**, *48*, 471–534. [CrossRef]

11. Yadav, N.; Seidi, F.; Crespy, D.; D'Elia, V. Polymers Based on Cyclic Carbonates as Trait D'Union Between Polymer Chemistry and Sustainable CO_2 Utilization. *ChemSusChem* **2018**. [CrossRef]

12. Bocqué, M.; Voirin, C.; Lapinte, V.; Caillol, S.; Robin, J.J. Petro-Based and Bio-Based Plasticizers: Chemical Structures to Plasticizing Properties. *J. Polym. Sci. Part A Polym. Chem.* **2016**, *54*, 11–33. [CrossRef]

13. Cacaval, D.; Blaga, A.C.; Cmru, M.; Galaction, A.I. Comparative Study on Reactive Extraction of Nicotinic Acid with Amberlite LA-2 and D2EHPA. *Sep. Sci. Technol.* **2007**, *42*, 389–401. [CrossRef]

14. Diniz, L.F.; Souza, M.S.; Carvalho, P.S.; da Silva, C.C.P.; D'Vries, R.F.; Ellena, J. Novel Isoniazid Cocrystals with Aromatic Carboxylic Acids: Crystal Engineering, Spectroscopy and Thermochemical Investigations. *J. Mol. Struct.* **2018**, *1153*, 58–68. [CrossRef]

15. Cokoja, M.; Bruckmeier, C.; Rieger, B.; Herrmann, W.A.; Kühn, F.E. Transformation of Carbon Dioxide with Homogeneous Transition-Metal Catalysts: A Molecular Solution to a Global Challenge? *Angew. Chemie Int. Ed.* **2011**, *50*, 8510–8537. [CrossRef]

16. Darensbourg, D.J. Making Plastics from Carbon Dioxide: Salen Metal Complexes as Catalysts for the Production of Polycarbonates from Epoxides and CO_2. *Chem. Rev.* **2007**, *107*, 2388–2410. [CrossRef] [PubMed]

17. Gao, W.Y.; Wu, H.; Leng, K.; Sun, Y.; Ma, S. Inserting CO_2 into Aryl C–H Bonds of Metal-Organic Frameworks: CO_2 Utilization for Direct Heterogeneous C–H Activation. *Angew. Chemie. Int. Ed.* **2016**, *55*, 5472–5476. [CrossRef]

18. León, T.; Correa, A.; Martin, R. Ni-Catalyzed Direct Carboxylation of Benzyl Halides with CO_2. *J. Am. Chem. Soc.* **2013**, *135*, 1221–1224. [CrossRef]

19. Mizuno, H.; Takaya, J.; Iwasawa, N. Rhodium(I)-Catalyzed Direct Carboxylation of Arenes with CO_2 via Chelation-Assisted C-H Bond Activation. *J. Am. Chem. Soc.* **2011**, *133*, 1251–1253. [CrossRef]

20. Schmeier, T.J.; Dobereiner, G.E.; Crabtree, R.H.; Hazari, N. Secondary Coordination Sphere Interactions Facilitate the Insertion Step in an Iridium(III) CO_2 Reduction Catalyst. *J. Am. Chem. Soc.* **2011**, *133*, 9274–9277. [CrossRef]

21. Yu, D.; Teong, S.P.; Zhang, Y. Transition Metal Complex Catalyzed Carboxylation Reactions with CO_2. *Coord. Chem. Rev.* **2015**, *293–294*, 279–291. [CrossRef]

22. Xie, J.N.; Yu, B.; Zhou, Z.H.; Fu, H.C.; Wang, N.; He, L.N. Copper(I)-Based Ionic Liquid-Catalyzed Carboxylation of Terminal Alkynes with CO_2 at Atmospheric Pressure. *Tetrahedron Lett.* **2015**, *56*, 7059–7062. [CrossRef]

23. Isse, A.A.; Ferlin, M.G.; Gennaro, A. Electrocatalytic Reduction of Arylethyl Chlorides at Silver Cathodes in the Presence of Carbon Dioxide: Synthesis of 2-Arylpropanoic Acids. *J. Electroanal. Chem.* **2005**, *581*, 38–45. [CrossRef]

24. Senboku, H.; Nagakura, K.; Fukuhara, T.; Hara, S. Three-Component Coupling Reaction of Benzylic Halides, Carbon Dioxide, and N,N-Dimethylformamide by Using Paired Electrolysis: Sacrificial Anode-Free Efficient Electrochemical Carboxylation of Benzylic Halides. *Tetrahedron* **2015**, *71*, 3850–3856. [CrossRef]

25. Cruz, H.; Gallardo, I.; Guirado, G. Electrochemically Promoted Nucleophilic Aromatic Substitution in Room Temperature Ionic Liquids-An Environmentally Benign Way to Functionalize Nitroaromatic Compounds. *Green Chem.* **2011**, *13*, 2531–2542. [CrossRef]

26. Dokania, A.; Ramirez, A.; Bavykina, A.; Gascon, J. Heterogeneous Catalysis for the Valorization of CO_2: Role of Bifunctional Processes in the Production of Chemicals. *ACS Energy Lett.* **2018**, *4*, 167–176. [CrossRef]

27. Isse, A.A.; Durante, C.; Gennaro, A. One-Pot Synthesis of Benzoic Acid by Electrocatalytic Reduction of Bromobenzene in the Presence of CO_2. *Electrochem. Commun.* **2011**, *13*, 810–813. [CrossRef]

28. Senboku, H.; Katayama, A. Electrochemical Carboxylation with Carbon Dioxide. *Curr. Opin. Green Sustain. Chem.* **2017**, *3*, 50–54. [CrossRef]

29. Zhao, G.; Huang, X.; Wang, X.; Wang, X. Progress in Catalyst Exploration for Heterogeneous CO_2 reduction and Utilization: A Critical Review. *J. Mater. Chem. A* **2017**, *5*, 21625–21649. [CrossRef]

30. Tahara, H.; Uranaka, K.; Hirano, M.; Ikeda, T.; Sagara, T.; Murakami, H. Electrochromism of Ferrocene and Viologen-Based Redox-Active Ionic Liquids Composite. *ACS Appl. Mater. Interfaces* **2018**, *11*, 1–6. [CrossRef]

31. Mao, X.; Wu, M.; Xu, X.; Jiang, L.; Yan, J.; Du, Z.; Li, J.; Hou, S. Fabrication of an Electrochemical Sensor for NO_x Based on Ionic Liquids and MoS_2. *Int. J. Electrochem. Sci.* **2018**, *13*, 11038–11048. [CrossRef]

32. Thompson, M.W.; Matsumoto, R.; Sacci, R.L.; Sanders, N.C.; Cummings, P.T. Scalable Screening of Soft Matter: Case Study of Mixtures of Ionic Liquids and Organic Solvents. *J. Phys. Chem. B* **2019**, *123*, 1340–1347. [CrossRef] [PubMed]

33. Reche, I.; Gallardo, I.; Guirado, G. Electrochemical Studies of CO_2 in Imidazolium Ionic Liquids Using Silver as a Working Electrode: A Suitable Approach for Determining Diffusion Coefficients, Solubility Values, and Electrocatalytic Effects. *RSC Adv.* **2014**, *4*, 65176–65183. [CrossRef]

34. Alvarez-Guerra, M.; Albo, J.; Alvarez-Guerra, E.; Irabien, A. Ionic Liquids in the Electrochemical Valorisation of CO_2. *Energy Environ. Sci.* **2015**, *8*, 2574–2599. [CrossRef]

35. Chong, F.K.; Andiappan, V.; Ng, D.K.S.; Foo, D.C.Y.; Eljack, F.T.; Atilhan, M.; Chemmangattuvalappil, N.G. Design of Ionic Liquid as Carbon Capture Solvent for a Bioenergy System: Integration of Bioenergy and Carbon Capture Systems. *ACS Sustain. Chem. Eng.* **2017**, *5*, 5241–5252. [CrossRef]

36. Gallardo, I.; Soler, S. Electrochemically Promoted Arylation of Iodoaromatics. *J. Electroanal. Chem.* **2017**, *799*, 9–16. [CrossRef]

37. Isse, A.A.; Falciola, L.; Mussini, P.R.; Gennaro, A. Relevance of Electron Transfer Mechanism in Electrocatalysis: The Reduction of Organic Halides at Silver Electrodes. *Chem. Commun.* **2006**, *1*, 344–346. [CrossRef]

38. Isse, A.A.; Gottardello, S.; Durante, C.; Gennaro, A. Dissociative Electron Transfer to Organic Chlorides: Electrocatalysis at Metal Cathodes. *Phys. Chem. Chem. Phys.* **2008**, *10*, 2409–2416. [CrossRef]

39. Isse, A.A.; Berzi, G.; Falciola, L.; Rossi, M.; Mussini, P.R.; Gennaro, A. Electrocatalysis and Electron Transfer Mechanisms in the Reduction of Organic Halides at Ag. *J. Appl. Electrochem.* **2009**, *39*, 2217–2225. [CrossRef]

40. Arnaboldi, S.; Bonetti, A.; Giussani, E.; Mussini, P.R.; Benincori, T.; Rizzo, S.; Isse, A.A.; Gennaro, A. Electrocatalytic Reduction of Bromothiophenes on Gold and Silver Electrodes: An Example of Synergy in Electrocatalysis. *Electrochem. commun.* **2014**, *38*, 100–103. [CrossRef]

41. Costentin, C.; Robert, M.; Savéant, J.-M. Catalysis of the Electrochemical Reduction of Carbon Dioxide. *Chem. Soc. Rev.* **2013**, *42*, 2423–2436. [CrossRef] [PubMed]

42. Gennaro, A.; Isse, A.A.; Save, J.; Severin, M.; Vianello, E.; Pado, V.; Loredan, V.; Diderot, D.; Cedex, P.; February, R.V.; et al. Homogeneous Electron Transfer Catalysis of the Electrochemical Reduction of Carbon Dioxide. Do Aromatic Anion Radicals React in an Outer-Sphere Manner? *J. Am. Chem. Soc.* **1996**, *118*, 7190–7196. [CrossRef]

43. Chang, M.M.; Saji, T.; Bard, A.J. Electrogenerated Chemiluminescence. 30. Electrochemical Oxidation of Oxalate Ion in the Presence of Luminescers in Acetonitrile Solutions. *J. Am. Chem. Soc.* **1977**, *99*, 5399–5403. [CrossRef]

44. Hayyan, M.; Mjalli, F.S.; Hashim, M.A.; AlNashef, I.M.; Mei, T.X. Investigating the Electrochemical Windows of Ionic Liquids. *J. Ind. Eng. Chem.* **2013**, *19*, 106–112. [CrossRef]