

1 Methanol electrosynthesis from CO₂ at Cu₂O/ZnO prompted 2 by pyridine-based aqueous solutions

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13 Abstract

14 In this study we examine the electrochemical-driven reduction of CO₂ to methanol at
15 Cu₂O/ZnO gas diffusion electrodes in soluble pyridine-based electrolytes at different
16 concentrations. The process is evaluated first by cyclic voltammetric analyses and then,
17 for the continuous reduction of CO₂ in a filter-press electrochemical cell. The results
18 showed that the use of pyridine-based soluble co-catalysts lowered the overpotential for
19 the electrochemical reduction of CO₂, enhancing also reaction performance (i.e. reaction
20 rate and Faradaic efficiency). Reaction outcome is discussed on the basis of the role that
21 N-ligands play on the mechanism and the inductive effect caused by the electron-
22 releasing or electron-withdrawing substituents of the aromatic ring.

23 In particular, the maximum methanol formation rate and Faradaic efficiency reached at
24 the 2-methylpyridine (with electron-releasing substituents)-based system with a pH of 7.6
25 and an applied current density of $j = 1 \text{ mA}\cdot\text{cm}^{-2}$ were $r = 2.91 \text{ }\mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ and $FE =$
26 16.86% , respectively. These values significantly enhance those obtained in the absence
27 of any molecular catalyst ($r = 0.21 \text{ }\mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ and $FE = 1.2\%$). The performance was
28 further enhanced when lowering the electrolyte pH by adding HCl ($r = 4.42 \text{ }\mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$
29 and $FE = 25.6\%$ at pH = 5), although the system showed deactivation in the long run (5 h)
30 which appears largely to be due to a change in product selectivity of the reaction (i.e.
31 formation of ethylene).

32 **Keywords:** Electrochemistry, CO₂ reduction, pyridine-based molecular catalysts, copper
33 oxide, methanol

34 1. Introduction

35 The idea that CO₂ can be captured [1-3] and reconverted to fuels in a Carbon Capture and
36 Utilisation (CCU) approach, sounds like a perfect solution that potentially could help to
37 solve global warming and energy shortage issues [4, 5]. Among the available technologies
38 for the activation and conversion of CO₂ into value-added chemicals [6], the
39 electrocatalytic alternative is appealing since it could enable an economically competitive
40 industrial production of CO₂-based fuels by using renewable energy [7, 8].

41 Moreover, from the spectrum of possible CO₂-reduced species, the formation of methanol
42 (CH₃OH) is of great interest since it is liquid at ambient conditions and can be readily
43 integrated into the existing liquid fuel transportation infrastructure [9, 10]. However, an
44 effective and selective production of CH₃OH (with 6 exchanged e⁻ required) by
45 electrochemical methods is a chemical challenge that still remains unsolved. Despite the
46 significant contributions that have been recently made in this reaction [9, 11-13], most of
47 the CO₂ electroreduction reports have been largely confined to 2 e⁻ products such as CO
48 and formate (HCOOH) and, in many cases, with low productivities. Besides, even though
49 proton-coupled electron transfers to CO₂ are thermodynamically facile, these reactions
50 require large overpotentials [9]. In order to help solving those limitations, organic
51 molecules have been found to be beneficial to promote the electrochemical reduction of
52 CO₂ [14, 15]. In particular, nitrogen-containing heterocycles such as pyridine (Py) appear
53 to lower overpotentials (indicating lower reaction barriers) and increase Faradaic
54 efficiencies (indicating higher selectivities toward CO₂ reduction products) in
55 electrochemical CO₂ conversion reactions as largely demonstrated by Bocarsly et al. [16-
56 22]. Their first results evidenced that CO₂ is catalyzed at hydrogenated Pd electrodes in
57 10 mM aqueous Py solutions [19, 22]. CH₃OH was detected with efficiencies up to 30%
58 at overpotentials of uniquely ~200 mV [22]. Py was found to act as electron shuttle
59 implying the formation of a carbamate as intermediate during the electron transfer to CO₂
60 [19]. In 2008, the same group exported this chemistry to a p-GaP photoelectrochemical
61 cell to yield 96% Faradaic efficiency (*FE*) for CH₃OH. They showed evidence of the key
62 role of Py to catalyze the selective formation of CH₃OH from CO₂ in a series of one-
63 electron steps at underpotentials of about 300 mV [21]. Based on the interesting results

64 for the electro-and-photoelectrocatalytic CO₂ reduction using Py developed by the group
65 of Bocarsly, recent reports from other groups have been advancing on the application of
66 Py-based molecular catalyst [23-29], demonstrating the benefits of using molecular
67 catalysts for the reduction of CO₂ to CH₃OH.

68 While the mechanisms of the reduction process seem to be still subject of debate, the
69 results clearly show that the identity of the soluble heterocycle and the metal electrode
70 influences the yield and product selectivity of the reaction [23, 30-34]. For example, the
71 use of Py with a p-GaP or a Pt cathode results in selective CH₃OH formation, while Py
72 with a Fe-pyrite cathode favours HCOOH production [15, 17, 22]. Among the available
73 catalytic materials, copper has been found to be unique to synthesize CH₃OH and >C1
74 hydrocarbons, such as ethanol and propanol [11-13, 35-37]. The performance of this
75 metal, however, generally implies large overpotentials and low selectivities [38].
76 Nevertheless, copper(I) oxide surfaces (i.e. Cu₂O) present both intermediate hydrogen
77 overpotentials and CO adsorption properties, which allows higher CH₃OH yields in
78 aqueous solutions to be produced [12, 13, 39-41]. Moreover, our previous work [13]
79 demonstrated that ZnO is able to stabilize Cu₂O in the hydrogenation reaction,
80 maintaining the stability of the catalyst for longer reaction times.

81 Therefore, with the present study we sought to address the use of Py-based aqueous
82 solutions for CO₂ conversion at Cu₂O/ZnO-based working electrodes. Previous works
83 have pointed that N-donor ligands like pyridine play a crucial role in the electron transfer
84 to CO₂ by forming a carbamate intermediate. Herein, a handful of pyridine derivatives
85 were used in this study in order to assess the inductive effect caused by electron-releasing
86 (*I*+) and electron-withdrawing (*I*-) substituents into the overall reaction outcome.
87 Precisely, we selected unsubstituted pyridine as reference and 2-methylpyridine, 4-
88 ethylpyridine, 2,4,6-trimethylpyridine, 2-chloropyridine, and 4,4'-bipyridine as
89 representative cases for *I*+ and *I*- effect. Influence of parameters such as Py type and its
90 concentration was preliminarily addressed by cyclic voltammetry. Thereafter, continuous
91 reduction of CO₂ to CH₃OH was conducted in a filter-press electrochemical cell at low
92 current densities ($j = 0.01 - 5 \text{ mA} \cdot \text{cm}^{-2}$) in a pH range from ca. 7.6 to 4.

93

94

95 2. Materials and methods

96 2.1. *Py*-based molecular catalysts

97 Pyridine (Py, 99%), 2-methylpyridine (2mPy, 98%), 4-ethylpyridine (4ePy, 98%), 2,4,6-
98 trimethylpyridine (246tmPy, 99%), 2-chloropyridine (2ClPy, 99%), and 4,4'-bipyridine
99 (44biPy, 99%) of reagent grade were used as commercially obtained. Figure 1 depicts the
100 selected pyridines, together with the pKa values of the corresponding pyridinium. It must
101 be noted that the pKa value can be correlated with inductive effect of the ring substituents.
102 When compared to the unsubstituted Py, the alkyl derivatives (2mPy, 246tmPy and 4ePy)
103 display an electron-releasing effect towards the N atom, making it a more basic position
104 (i.e. a greater pKa of the pyridinium). 44biPy and 2ClPy exhibit somewhat lower and
105 markedly lower pKa values according to their mild and strong electron-withdrawing
106 effects. These features will be considered in the discussion section, as they are also closely
107 related to the ability of the pyridinic ring to mediate the electron transfer through the
108 formation of a carbamate intermediate by the nucleophilic addition to CO₂.

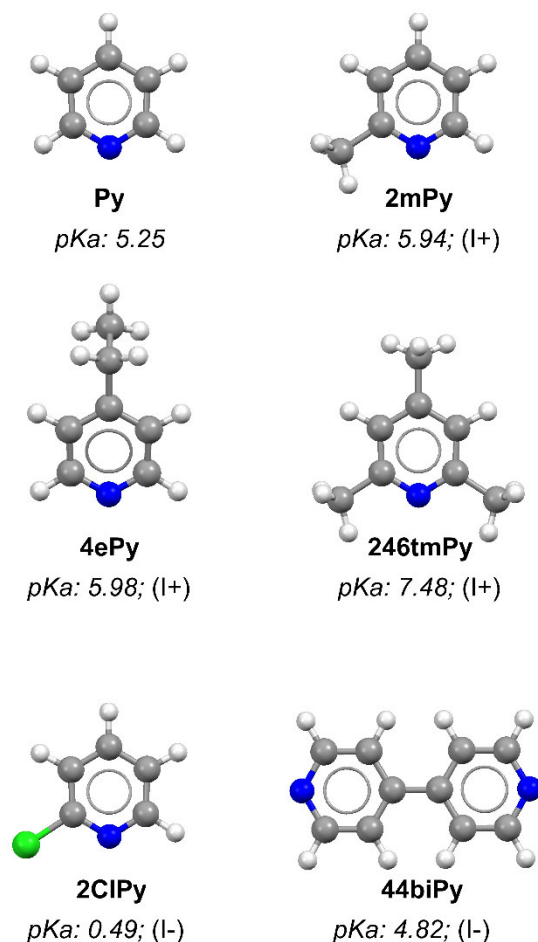


Figure 1. Selected pyridines (colour codes: C grey, H white, N blue, and Cl green) including *pKa* values of the corresponding pyridinium. Nature of the inductive effect in parentheses.

109

110 2.2. Cyclic voltammetry characterization

111 The electrochemical behaviour was evaluated with a PGSTAT 302N potentiostat
 112 (Metrohm, Autolab B.V.) under GPES software control employing a conventional three
 113 electrode electrochemical cell. A glassy carbon and Ag/AgCl (sat. KCl) were used as a
 114 counter and reference electrode, respectively. Portions of the Cu₂O/ZnO-based materials
 115 were used as cathodes. The aqueous electrolyte (0.5 M KHCO₃) containing the different
 116 molecular catalysts at different concentrations (i.e. 10, 25 and 50 mM) was saturated with
 117 ultrapure CO₂ (99.99%) by bubbling for 20 min before the tests. The current-voltages
 118 curves were obtained with a scan rate of 50 mV·s⁻¹ at potentials ranging from 0 to -1.2 V
 119 vs. Ag/AgCl. Current density is expressed as the total current divided by the geometric
 120 surface area, A, of the electrodes.

121 2.3. Electrochemical cell for CO₂ reduction

122 The continuous electrochemical measurements for CO₂ reduction were carried out in a
123 filter-press electrochemical cell (Micro Flow Cell, ElectroCell A/S) at ambient
124 conditions. A cation exchange membrane (Nafion[®] 117) separated the cathode and anode
125 compartments of the cell. The membrane presented a phase-segregated structure that
126 allows the selective transport of H⁺ ions from the anode to the cathode chamber with a
127 low permeability to CH₃OH [42]. A platinised titanium electrode was used as a counter
128 electrode and Ag/AgCl (sat. KCl), assembled close to the cathode, was used as reference
129 electrode. The Cu₂O/ZnO-catalyzed carbon papers were employed as working electrodes
130 (A= 10 cm⁻²). The preparation of the Cu₂O/ZnO electrodes has been described in detail
131 in our previous works [12, 13]. Basically, Cu₂O (Sigma Aldrich, particle size < 5 μm,
132 97% purity) and ZnO particles (ACROS organic, < 45 μm, 99.5%) were mixed with a
133 Nafion[®] dispersion 5 wt.% (Alfa Aesar) and isopropanol, IPA (Sigma Aldrich), with a
134 70/30 catalyst/Nafion mass ratio and a 3% solids (catalyst + Nafion). The ink was
135 airbrushed onto a porous carbon paper (TGP-H-60, Toray Inc.) to form a gas diffusion
136 electrode (GDE) with a catalytic loading of 1 mg·cm⁻². All electrodes were dried and
137 rinsed with deionised water before use.

138 The filter-press electrochemical system possesses three inputs (catholyte, anolyte and
139 CO₂ separately) and two outputs (catholyte-CO₂ and anolyte). The GDE cell
140 configuration allows the electroreduction of CO₂ supplied directly in gas phase [12, 43,
141 44]. The cathode side of the reactor was fed with CO₂ gas (99.99%) with a flow/area ratio
142 of $Q_g/A = 20 \text{ ml}\cdot\text{min}^{-1}\cdot\text{cm}^{-2}$, adjusted by a rotameter. A 0.5 M KHCO₃ (Panreac, >97%
143 purity) aqueous solution containing different concentrations of the Py-based molecular
144 catalysts (i.e. 10, 25 and 50 mM) was used as catholyte. The anolyte was a 0.5 M KHCO₃
145 aqueous solution. Prior to the experiments, the aqueous electrolyte was saturated with
146 CO₂ by bubbling for 20 min. The pH of the saturated solution was measured with a pH-
147 meter PH 25 (Crison, PAIS). The pH before the tests was adjusted to 4, 5 and 6 by adding
148 HCl (Panreac, 37%).

149 The electrolytes were pumped from catholyte and anolyte tanks to the cell by two
150 peristaltic pumps (Watson Marlow 320, Watson Marlow Pumps Group) at a flow rate of
151 $Q_e/A = 1 \text{ ml}\cdot\text{min}^{-1}\cdot\text{cm}^{-2}$. The experiments were performed at galvanostatic conditions in a
152 current density range of $j = 0.05 - 5 \text{ mA}\cdot\text{cm}^{-2}$, using an AutoLab PGSTAT 302N

153 potentiostat (Metrohm, Autolab B.V.) The experimental time was 90 min, where pseudo-
154 stable conditions are reached [12, 13]. Liquid samples were taken every 15 min from the
155 catholyte tank.

156 The concentration of products in each sample was analysed by duplicate in a headspace
157 gas chromatograph (GCMS-QP2010 Ultra Shimadzu) equipped with a Flame Ionization
158 Detector (FID). Compounds were separated on a DB-Wax 30 m x 0.25 mm x 0.25 μm
159 column, with an injection and detector temperature of 250 $^{\circ}\text{C}$ and 270 $^{\circ}\text{C}$, respectively.
160 Helium was used as a carrier gas at a flow rate of 50 $\text{ml}\cdot\text{min}^{-1}$. The identification of
161 obtained products was further confirmed by headspace gas chromatography-mass
162 spectrometry (GCMS-N5975B) using a 60 m x 250 μm x 1.40 μm DB-624 capillary
163 column. An averaged concentration was obtained for each point from the performance of
164 three separate runs with an experimental error less than 17.3%.

165 The performance of the process is evaluated by the rate of CH_3OH production, r (i.e.
166 CH_3OH obtained per unit of cathode area and time), and the FE (i.e. selectivity of the
167 reaction to produce CH_3OH). FE is calculated assuming that 6 e^- are required per
168 molecule of CH_3OH .

169 **3. Results and discussion**

170 *3.1. Cyclic voltammetric analyses*

171 Figure 2a reveals the current-voltage response after 5 electrochemical scans for the
172 $\text{Cu}_2\text{O}/\text{ZnO}$ GDEs in a CO_2 -saturated 0.5 M KHCO_3 aqueous solution, and the response
173 upon adding 25 mM concentration of 2mPy in the electrolyte solution. This Py-based co-
174 catalyst was firstly selected due to its ability to significantly reduce the activation
175 overpotential (i.e. its role in the activation energy due to electron transfer) for CO_2
176 reduction [45]. The results are compared to those responses obtained at a Cu plate. To
177 further analyse the activity for CO_2 reduction, Figure 2b shows the curves for $\text{Cu}_2\text{O}/\text{ZnO}$
178 and Cu electrodes under CO_2 and N_2 saturation. Current densities, j , are normalized to the
179 geometric area (A) of the electrodes.

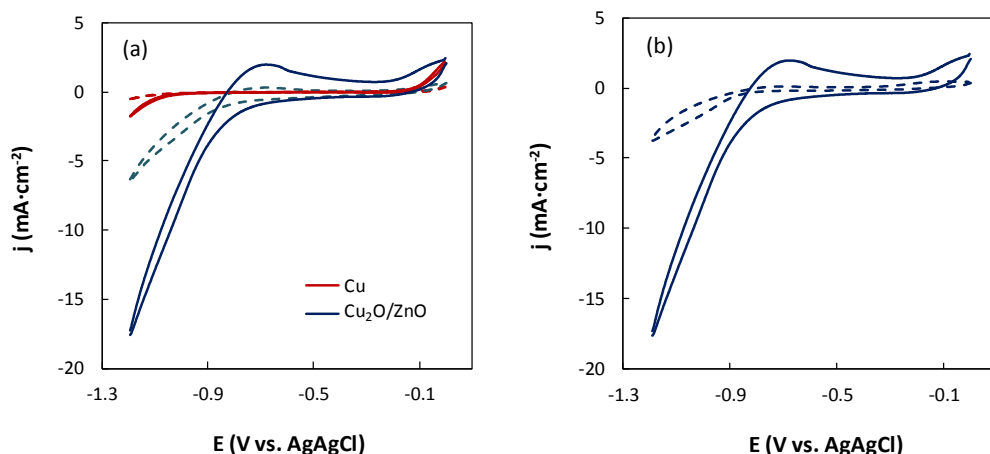


Figure 2. Cyclic voltammograms for: (a) Cu₂O/ZnO and Cu-based systems in CO₂-saturated 0.5 M KHCO₃ aqueous electrolytes in the presence and absence (dotted line) of 2mPy (25 mM) and, (b) Cu₂O/ZnO in CO₂ and N₂ (dotted line) saturated 0.5 M KHCO₃ + 2mPy (25 mM) solution.

180

181 Figure 2a shows that higher activities are reached for both Cu-based catalysts by
 182 employing Py-based molecular co-catalysts, as denoted by the large differences between
 183 voltammetry profiles in the absence/presence of 2mPy solubilised in the electrolyte. In
 184 fact, a very remarkable enhancement can be obtained in case of incorporating 25 mM of
 185 2mPy in the Cu₂O/ZnO-based system, denoting the synergic co-catalytic effect of copper
 186 oxide species and Py in the activity response, in contrast with the restricted improvements
 187 at the Cu plate in the absence/presence of the molecular catalyst.

188 The main characteristic of the voltammograms is a reduction process starting at around -
 189 0.8 V vs. Ag/AgCl, which can be initially associated with the reduction of CO₂ and partial
 190 formation/decomposition of the oxides at the electrode surface. The oxidative peak at -
 191 0.7 V in the reverse scan of Cu₂O/ZnO curves might be initially assigned to the transition
 192 of remaining Zn to ZnO. However, the peak remains after the fifth scan, and so it probably
 193 has more to do with the formation of oxidized subproducts in the CO₂ reduction reaction.
 194 In addition, the curves in Figure 2b show that in the presence of both, 2mPy and CO₂, a
 195 substantial enhancement of the reduction wave, in comparison to that response in a N₂-
 196 saturated solution, was observed at more negative potentials than -1 V. Thus, this
 197 reduction peak is mainly attributed to CO₂ reduction rather than the oxidation-reduction
 198 of the catalytic materials. In fact, the reduction response occurs at around 200 mV lower
 199 overpotential in the presence of pyridine (compared to the system with a CO₂-saturated
 200 electrolyte without 2mPy). This denotes the important co-catalyst and synergic effect of
 201 2mPy in the reduction of CO₂.

202 For the sake of evaluating the effect of the electron-releasing ($I+$) or electron-
 203 withdrawing ($I-$) character on CO_2 reduction activity, cyclic voltammograms were
 204 acquired for the other Py derivatives (i.e. 4ePy, 246tmPy, 2ClPy, 44biPy) in a
 205 concentration of 25 mM (Figure 3a). The results are compared to the electrochemical
 206 activity of unsubstituted Py as a reference. Besides, Figure 3b shows the effect of adding
 207 different concentrations of 2mPy (i.e. 10, 25 and 50 mM) in the CO_2 reduction response.

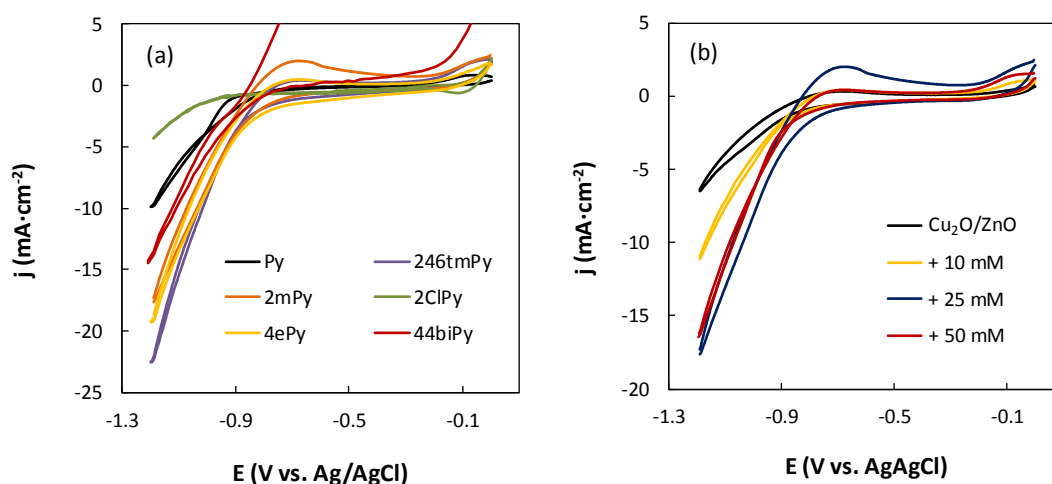


Figure 3. Cyclic voltammograms for $\text{Cu}_2\text{O}/\text{ZnO}$ GDEs in a 0.5 M KHCO_3 aqueous solution containing: (a) 25 mM of the different Py-based molecular catalyst and, (b) different concentrations of 2mPy molecular catalyst (i.e. 10, 25 and 50 mM).

208

209 Compared to the reference Py, substituted ones show accused shifts on either onset of the
 210 reduction wave (i.e. lower activation overpotential) and its intensity. The lowering of the
 211 overpotential observed for 2mPy, 4ePy and 246tmPy can be rationalized by the electron
 212 releasing short alkyl groups ($I+$ effect). This makes the Py-N atom a better σ -donor and
 213 thus, more prone to form the carbamate through an addition reaction to the electrophilic
 214 C atom and, ultimately, to transfer the electron to CO_2 .

215 On the contrary, the presence of a strong inductively electron-withdrawing group ($I-$
 216 effect) on the *ortho* substituted 2ClPy, worsens σ -donor ability of N atom and hinders
 217 somewhat the formation of the carbamate and the resulting electron transfer. As a result,
 218 its voltammogram reveals a reduced current intensity and a shift towards greater
 219 overpotentials compared to referential Py. In the case of 44biPy, despite a slight
 220 worsening of the activity might be expected according to its moderate $I-$ effect, its onset
 221 is somewhat lower than that of Py. Such behaviour might be attributed to the presence of
 222 two aromatic rings and two equivalent σ -donor N-atoms per molecule ready to transfer

223 two electrons. It is noticeably that the marked oxidation peak found for the
224 voltammogram measured in presence of 44biPy points to the formation and subsequent
225 oxidation of reduced intermediates different to those rendered by other pyridinic co-
226 catalysts (i.e. a change in selectivity). This fact can be also related to the ability of 44biPy
227 to promote 2 e- transfer which would imply mechanistic changes (see Figure S1 in
228 Supplementary information). In any case, apart of influencing in the CO₂ reduction, it
229 must be considered that Py ring mediated electron transfer prompts also the catalytic
230 generation of hydrogen [46], being also responsible of the reduction wave behaviour. This
231 process follows also the above described trend, as the *I*+ effect caused by electron
232 releasing groups leads to more basic N atom (higher pKa of the corresponding
233 pyridinium), resulting in a molecular catalyst more prone to bind a proton and transfer
234 the electron.

235 Moreover, Figure 3b demonstrated that with increases in Py ions in the solution, the
236 catalytic current-response is enhanced up to a concentration of 25 mM. Further increases
237 in concentration did not lead to higher voltammetric responses. Hence, the redox CO₂
238 reaction is limited by the high concentration of Py, suggesting that CO₂ has become the
239 limiting reagent as the concentration of Py increases [18, 26].

240 3.2. Filter-press electrochemical cell

241 To further explore the performance of these co-catalysts, Table 1 presents the data for the
242 continuous transformation of CO₂ in the filter press electrochemical cell equipped with a
243 Cu₂O/ZnO GDE and the Py derivatives tested at different concentrations (i.e. 10, 25 and
244 50 mM) in the supporting electrolyte (0.5 M KHCO₃). The results are compared with
245 those obtained in the absence of any Py molecular catalyst. The pH of the electrolytes
246 ranged from 6.8 to 7.6 on dependence of the Py-based co-catalyst applied. The analysis
247 is carried out in terms of *r* and *FE* at a low current density ($j= 1 \text{ mA}\cdot\text{cm}^{-2}$) where a better
248 CO₂ electroreduction performance is expected in Py-based CO₂ co-catalyzed reactions
249 [45].

250 The electroreduction process led to CH₃OH formation, with also traces of C₂H₅OH, in
251 accordance to previous results at copper oxides surfaces [9, 21, 22] and recent reports on
252 the application of pyridines for CO₂ electroreduction [27-29]. No other liquid products
253 were detected. Control experiments for the reduction of CO₂ at low overpotentials

254 catalyzed by the carbon paper (without sprayed Cu₂O/ZnO particles) did not produce any
 255 measurable liquid product.

256 **Table 1.** *r* and *FE* at Cu₂O/ZnO in the presence/absence of Py-based co-catalysts at different
 257 concentrations. *j*= 1 mA·cm⁻², *Q_e/A*= 1 ml·min⁻¹·cm², *Q_g/A*= 20 ml·min⁻¹·cm².

<i>Molec. Catalyst (substituents)</i>	<i>Py conc.</i> , mM	<i>E</i> , V vs. Ag/AgCl	<i>r</i> , μmol·m ⁻² ·s ⁻¹	<i>FE</i> , %
-	-	-1.35	0.21	1.2
Py	10	-1.21	2.6	15.06
	25	-1.24	2.24	12.95
	50	-1.17	0.94	5.42
2mPy (<i>I</i> +))	10	-1.03	2.91	16.86
	25	-1.12	1.98	11.44
	50	-1	1.46	8.43
4ePy (<i>I</i> +))	10	-1.02	1.35	7.83
	25	-0.95	1.2	6.93
	50	-1.14	0.73	4.22
246tmPy (<i>I</i> +))	10	-0.94	2.18	12.65
	25	-0.99	2.24	12.95
	50	-1.03	1.51	8.73
2ClPy (<i>I</i> -))	10	-1.41	0.73	4.22
	25	-1.41	0.78	4.52
	50	-1.15	0.42	2.41
44biPy (<i>I</i> -))	10	-1.16	0.26	1.51
	25	-1.21	0.21	1.20
	50	-1.19	0.16	0.90

258
 259 The results indicated that by employing Py-based co-catalysts, an enhancement in
 260 CH₃OH formation rates was observed in all cases, with values in general notably higher
 261 than those obtained at Cu₂O/ZnO GDEs in the absence of Py (*r*= 0.21 μmol·m⁻²·s⁻¹)
 262 independently of the Py concentration applied. Besides, the cathodic voltages were in
 263 general more positive in case of adding Py-based molecular catalysts than those results
 264 in the absence of Py, being in concordance with the role that Py co-catalysts play in the
 265 electron transfer. For example, at an applied constant current of *j*= 1 mA·cm⁻² (*E*=- 1.03
 266 V vs. Ag/AgCl), an averaged *FE* for CH₃OH formation of 16.86% was observed with
 267 2mPy (10 mM) as co-catalyst. Significantly higher voltage (*E*= -1.35 V vs. Ag/AgCl) was
 268 required under similar conditions in the absence of Py and only a *FE*= 1.2% was achieved.
 269 Moreover, the relative overpotential lowering follows the same trend that the one
 270 observed from cyclic voltammetric analyses (Figure 3a), according to the inductive effect
 271 caused by the substituents (see discussion in Section 3.1). Only 2ClPy shows an
 272 overpotential comparable to that provided by the Cu₂O/ZnO in the absence of co-catalysts,

273 indicating that electron-withdrawing effect caused by the Cl⁻ substituent renders Py ring
274 less active towards electron transfer (see above discussion).

275 As a rule, the lower voltages required in the Py-based co-catalysts are consistent with the
276 faster kinetics to produce CH₃OH. The enhanced production rate is evident from
277 comparison of $r = 2.91 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ obtained at 2mPy (10mM)-based system, which is an
278 order of magnitude higher than $r = 0.21 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ in the absence of Py. Therefore, Py-
279 based co-catalysts are able to reach higher r and FE at lower cathode potentials. Despite
280 the relative low yields, the FE results are comparable to recent results (4-35%) for the use
281 of pyridinium (protonated Py) and related aromatic nitrogen-heterocycles as
282 electrocatalysts for CH₃OH production [28, 29, 47-49]. Despite Py derivatives cause, in
283 general, an improvement in r and FE , the results do not match the expectations
284 considering only the inductive effect. For instance, the overpotential reduction caused by
285 $I+$ substituents is not strictly correlated with the CH₃OH production rate and Faradaic
286 efficiency, since 4ePy and 246tmPy co-catalysts, possessing electron-releasing groups,
287 reduce the overpotential with respect the unsubstituted Py, but lead to slightly worse r
288 and FE values, which is probably due to the complexity of the multiple steps involved,
289 stability of the intermediates and the formation of non-liquid subproducts [19, 46].
290 Further evidences are inferred from the case of 44biPy, that sets an overpotential
291 comparable to referential Py, but leads to r and FE values as low as those provided in
292 absence of co-catalyst. Again, such efficiency lowering is attributable to a change in
293 product selectivity as previously inferred from the anomalous peak observed in the
294 voltammogram for 44biPy (Figure 3a).

295 Increase in pyridine concentration from 10 to 25 mM led to a noticeable lower CO₂
296 conversion performance. These results are unexpected according to the higher CO₂
297 reduction activity observed from cyclic voltammetric analyses (Figure 3b), but agree well
298 with previous observations, where redox CO₂ reactions were found to be limited at high
299 concentrations of Py. Apparently, as pointed in the previous section, availability of CO₂
300 is the limiting factor, in such a way that an excess of Py co-catalyst can induce the
301 catalytic generation of H₂ [46], resulting in lower r and FE for CH₃OH. In particular, a
302 recent report for the photocatalytic reduction of CO₂ in Ru-phenanthroline complex
303 photosensitizers, concluded that when Py concentration was higher than 6.35 mM,
304 another unidentified redox reaction, apart from the conversion of CO₂ to CH₃OH, took
305 place [50]. Further increases in molecular catalyst concentration led to a drastic reduction

306 in CH₃OH yield and *FE*, which can be explained by a combination of CO₂ and proton
 307 reduction, the latter process dominating as the concentration of pyridinium increased [18].
 308 Overall, the results denoted the benefits of using a Cu₂O/ZnO-Py-based system with an
 309 optimum molecular catalyst concentration of 10 mM for the electroreduction of CO₂,
 310 although the results for CH₃OH concentration are limited to a sub-mg·L⁻¹ level,
 311 irrespectively of the Py-based co-catalyst concentration.

312 In order to identify kinetic limitations for CH₃OH formation, Figure 4 presents the
 313 production rate and selectivity for CH₃OH formation in a current density range of $j= 0.05$
 314 - $5 \text{ mA}\cdot\text{cm}^{-2}$ for the 2mPy (10 mM)-based system, where the best performance can be
 315 achieved.

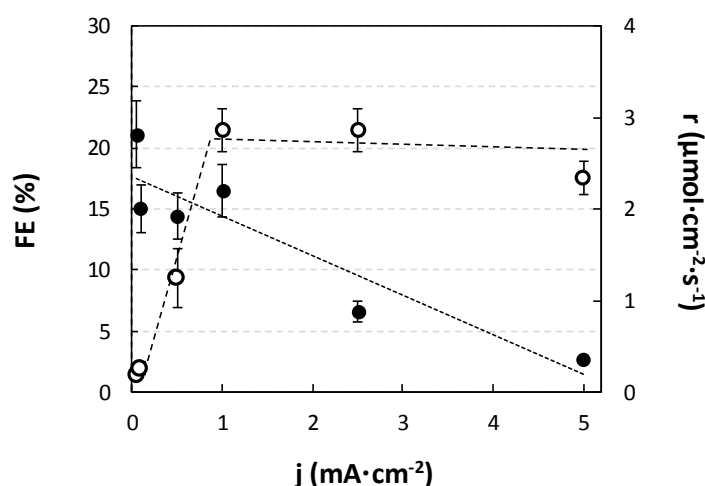


Figure 4. r (○) and FE (●) for Cu₂O/ZnO-2mPy (10 mM)-based system in a current density range of $j= 0.05 - 5 \text{ mA}\cdot\text{cm}^{-2}$.

316 The figure shows that *FE* for CH₃OH generally increased as the current density lowered.
 317 The same was observed by Barton et al. [21] and Frese et al. [51], where *FE* for CH₃OH
 318 increased as current density was reduced at Ga-based electrodes, due to the competing H₂
 319 evolution in conjunction with CO₂ reduction. The same was recently reported by
 320 Rybchenko with Pt electrodes at high CO₂ pressure [27]. On the other hand, CH₃OH
 321 production rate is remarkably reduced at low current densities ($j= 0.05 - 0.5 \text{ mA}\cdot\text{cm}^{-2}$)
 322 but then remains almost invariable at increasing currents ($j= 1 - 5 \text{ mA}\cdot\text{cm}^{-2}$), indicating a
 323 reaction-limited rate. Overall, with 2mPy as soluble electrocatalyst and a semi-optimum
 324 current density of $j= 1 \text{ mA}\cdot\text{cm}^{-2}$ the performance of the Py-co-catalyzed process seems to
 325 be enhanced.
 326

327

328 3.3. Influence of pH and long-term stability

329 Previous literature demonstrated that CO₂ reduction is enhanced by pyridinium in aqueous
 330 solutions of pH ranging from 5.2 to 5.4 [19, 22, 23, 29, 47, 49, 52], which can be related
 331 to the pK_a of Py [53]. It seems that at these pH conditions pyridinium exists in a higher
 332 concentration than the free proton, enabling the Py to function as proton source ([PyH⁺])
 333 as well as intermediates stabilizer via hydrogen bonding, enhancing also catalytic current
 334 [26, 30]. Table 2 shows the quantitative information (*r* and *FE*) regarding the production
 335 of CH₃OH at a pH ranging from 4 to 6 in the Cu₂O/ZnO-2mPy (10 mM) system. The pH
 336 was adjusted by adding HCl to the solution. Trace amounts of C₂H₅OH were also
 337 detected. The values are compared to the performance found at a pH of 7.6.

338 **Table 2.** *r* and *FE* at Cu₂O/ZnO-2mPy (10mM) for a pH range of 4 -7.6. *j* = 1 mA·cm⁻². *Q_g/A* = 1 ml·min⁻¹·cm⁻², *Q_g/A* = 20 ml·min⁻¹·cm⁻²

pH	<i>E</i> , V vs. Ag/AgCl	<i>r</i> , μmol·m ⁻² ·s ⁻¹	<i>FE</i> , %
7.6	-1.03	2.91	16.86
4	-0.59	2.18	12.65
5	-0.62	4.42	25.6
6	-0.84	3.28	18.97

340

341 As observed, a mild acidification (pH= 5-6) led to increases in CH₃OH production,
 342 indicating that reaction kinetics depend on the concentration of pyridinium ions ([PyH⁺])
 343 and/or hydrons available in the solution [26, 54, 55]. In fact, the marked lowering in the
 344 overpotential points to a change in the reaction mechanism which necessarily needs to go
 345 by a different transition state as the protonated pyridinium cannot directly form the
 346 carbamate [19]. Specifically, the rate for CH₃OH formation is as high as *r*= 4.42 μmol·m⁻²·s⁻¹
 347 at an optimum pH value of 5, which is around 1.5 times higher than the production
 348 rate observed for Cu₂O/ZnO-2mPy (10 mM) at pH=7.6. In the same manner, the
 349 efficiency of the process is significantly raised by reducing the pH of the solution, with a
 350 value as high as *FE*= 25.6% for an applied voltage of *E*= -0.62 V vs. Ag/AgCl (*j*= 1
 351 mA·cm⁻²), thus corresponding to a overpotential of ca. 150 mV more than the
 352 thermodynamic potential needed for CH₃OH formation (-0.47 V vs. Ag/AgCl) at pH of
 353 5.4 [22]. It is important to note that the reaction outcome improvement can be also
 354 attributed to the partial dissolution of ZnO at mild acidic pHs, which would render more

355 Cu₂O exposed at the surface of the cathode. It is also noteworthy to mention that this *FE*
 356 to CH₃OH formation is comparable to that maximum value obtained in our previous
 357 report for the same Cu₂O/ZnO-based catalyst in the absence of any Py molecular catalyst
 358 ($FE_T= 27.5\%$) [12], although in this latter a current density of $j= 10 \text{ mA}\cdot\text{cm}^{-2}$ was
 359 required. This indicates the relevance of using Py-based molecular catalysts to enhance
 360 the energy efficiency of the electrocatalytic reduction of CO₂.

361 Further reductions in pH to 4 produced a severe decrease in process efficiency, which
 362 could be initially interpreted by reductions in CO₂ solubility when decreasing the pH [18,
 363 54]. Nonetheless, previous reports demonstrated the formation of copper(I) chloride
 364 (CuCl) in the presence of HCl when evaluating Cu-based electrocatalysts for CO₂
 365 reduction [56]. CuCl compound has been proven to preferentially promote the formation
 366 of ethylene (C₂H₄) from the electrocatalytic reduction of CO₂, due to the ability of CuCl
 367 to reversibly combine with CO and C₂H₄ [56]. This will also explain the drastic reduction
 368 in *FE* to CH₃OH observed at pH= 4.

369 Finally, an evaluation of the Cu₂O/ZnO-2mPy (10 mM)-based system performance for
 370 CO₂ electroreduction at ambient conditions is evaluated in the long-run (5 h). The results
 371 for *r* and *FE* evolution are presented in Figure 5a and Figure 5b in a pH of 7.6 and 5,
 372 respectively. The stability of the co-catalyzed reduction was tracked while continuously
 373 sparging the solution with CO₂ at a constant current density of $j= 1 \text{ mA}\cdot\text{cm}^{-2}$, where a
 374 good balance between *FE* and *r* is observed (Figure 4, Table 1).

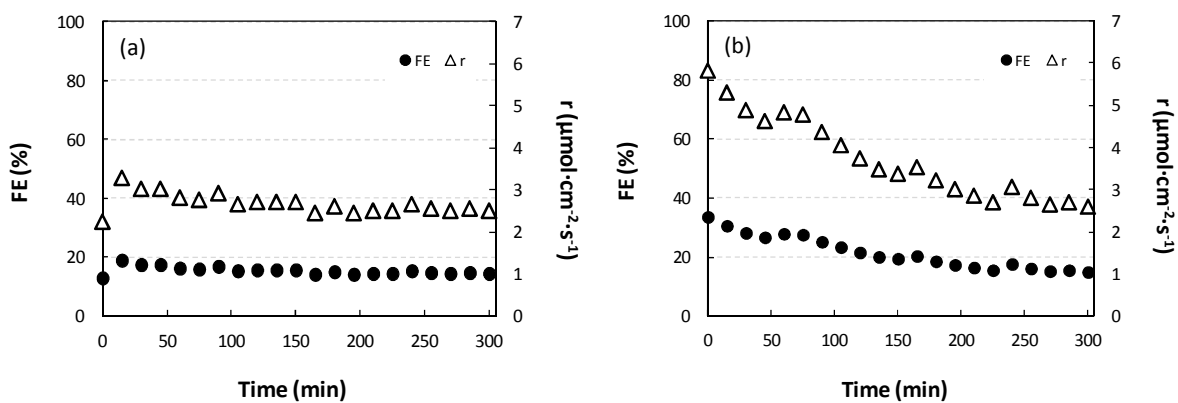


Figure 5. Time-dependence on *r* and *FE* for the Cu₂O/ZnO-2mPy (10 mM)-based system at (a) pH= 7.6 and (b) pH=5. $j=1 \text{ mA}\cdot\text{cm}^{-2}$, $Q_e/A= 1 \text{ ml}\cdot\text{min}^{-1}\cdot\text{cm}^{-2}$, $Q_g/A= 20 \text{ ml}\cdot\text{min}^{-1}\cdot\text{cm}^{-2}$.

375

376 As observed, the Cu₂O/ZnO-2mPy (10mM)-based system (pH= 7.6) showed only a slight
 377 activity decrease in the long run with a CH₃OH formation rate of $r= 2.5 \text{ }\mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ and

378 $FE= 14.45\%$ at the end of the test (Figure 5a). We speculate that pairing a Py-based co-
379 catalyst with a Cu_2O/ZnO cathode could potentially mitigate the limited stability
380 observed in the electroreduction of CO_2 for CH_3OH production [9]. In fact, previous
381 literature demonstrated that a stable electroreduction of CO_2 to $HCOOH$ over 5 days can
382 be reached at Sn-2mPy-based electrocatalytic system for a current applied of $j= 1\text{ mA}\cdot\text{cm}^{-2}$
383 in a membrane-separated cell [45]. In contrast, when the pH decreased to 5 (by the
384 addition of HCl) a significant drop in process performance is clearly observed at the initial
385 3 h of experimental time with a 49% loss of activity (Figure 5b). Then, the production
386 seems to slightly decrease (or stabilize) until the end of the test ($r= 2.6\text{ }\mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$, $FE=$
387 15.1%). In fact, the FE after 5 h is similar to that steady-state value observed for a pH =
388 7.6 ($FE= 14.45\%$), which may probably indicate that the process performance is limited
389 by the pyridine- Cu_2O/ZnO combination itself, rather than the pH of the electrolyte
390 solution.

391 This reduction in process performance at pH= 5 is unexpected if we observe the stable
392 CH_3OH formation rates reached at long reactions times in photo-and-electrocatalytic
393 systems based on Ga, Pd and Ru metals at a similar pH level [21, 25, 26]. For example,
394 Barton et al. found that the production of CH_3OH was linear with a charge passed ranging
395 from 3 to 10 C at pH= 5.2 and 7 h of operation using a p-GaP-based photo-electrochemical
396 cell. The Py concentration was also observed to be invariant over the time of the
397 experiments, indicating that it is not consumed by the CH_3OH formation reaction [21]. In
398 the same manner, Wang et al. [26] observed a stable production of CH_3OH , as solo
399 product, from CO_2 in aid of Ru-phenanthroline complex photosensitizer. The yield of
400 CH_3OH reached $60\text{ }\mu\text{mol}\cdot\text{L}^{-1}$ after 6 h of reaction time. Literature shows, however, that
401 certain metals, such as Zn [57] and Cu [58], corrode more easily and give up electrodes
402 when exposed to an acidic solution, which lead to a reduced performance. From our
403 analyses a striking feature is that cathodic voltage rose only slightly after 5 h of
404 electrolysis, from -0.62 V (after 15 min.) to -0.76 V vs. Ag/AgCl to maintain a current
405 density of $j= 1\text{ mA}\cdot\text{cm}^{-2}$ (Figure 5b). This limited increase in potential over time can be
406 attributed to the consumption of the acid during the reduction process [47], since the pH
407 of the aqueous electrolyte solutions increased from 5 to 5.69 after electrolysis. In any case,
408 the limited increase in E probably indicate that the electrocatalytic system maintains its
409 CO_2 reduction activity after 5 h of operation and thus, we hypothesized that the reduction
410 in r and FE to CH_3OH observed has probably more to do with a variation in product

411 selectivity (C_2H_4 formation with CuCl) [56], rather than the degradation of the catalytic
412 material in the presence of HCl. Overall, the stable formation of CH_3OH at the
413 Cu_2O/ZnO -2mPy (10 mM)-based system at a pH of 7.6, with a $FE= 14.45\%$ and moderate
414 $r= 2.5 \mu mol \cdot m^{-2} \cdot s^{-1}$, show the potential of using Py-based molecular catalyst in the
415 electroreduction of CO_2 to CH_3OH .

416 The outstanding scientific challenge seems to be in the understating of the underlying
417 reaction mechanisms of Py-catalyzed CO_2 reduction processes to form CH_3OH , not only
418 to exhaustively elucidate the role of Py but also to develop related catalysts that exploit
419 the fundamental phenomena at play in the reduction reaction. It is suggested that the
420 reduction mechanisms of the reduction proceed through various coordinative interactions
421 between the Py radical and CO_2 to form carbamate-like species, which are proposed to be
422 the rate determining step for the process [18, 59], and then a subsequent sequential
423 electron and proton transfer processes to ultimately yield CH_3OH . In the current work,
424 the inductive effect caused by the electron-withdrawing and releasing substituents on σ -
425 donor N atom of the Py ring seems to play an important role in the electron transfer to
426 CO_2 and thus, in the reaction outcome. However, there is a delicate balance between
427 kinetics and thermodynamics underlying the observed reactivity. While increased
428 electron-releasing ability of the Py-based molecular catalyst is predicted to favour the
429 electron transfer to the electrophilic C atom of the CO_2 and increase reaction rate
430 corresponding to this stage, at the same time this would also stabilize the carbamate
431 species, which is not desired for the subsequent CH_3OH formation [18]. Certainly, further
432 experimental work is required to fully elucidate CO_2 reduction steps to CH_3OH in the Py-
433 based catalysed reaction, including the analysis of charge-transfer processes and the
434 governing physical and chemical phenomena taking place in the electrochemical systems
435 [60], although significant research efforts have been recently made [16, 26, 30-32, 54, 61-
436 66].

437 **4. Conclusions**

438 This work demonstrated the beneficial use of pyridine-based molecular catalysts
439 containing electron-releasing or electron-withdrawing groups (i.e. 2-methylpyridine, 4-
440 ethylpyridine, 2,4,6-trimethylpyridine, pyridine, 2-chloropyridine, 4,4-bipyridine), to
441 reach enhanced energy efficiencies for the electrocatalytic reduction of CO_2 to methanol
442 at Cu_2O/ZnO -based surfaces.

443 The results showed that all the applied pyridine-based soluble co-catalysts lowered the
444 overpotential for the electrochemical reduction of CO₂. In particular, the reduction
445 response occurred at around 200 mV lower overpotential in the presence of 2-
446 methylpyridine (compared to the electrocatalytic system with a CO₂-saturated electrolyte
447 without it). The overpotential reduction with respect to the unsubstituted Py is explained
448 by electron-releasing alkyl groups (*I+ effect*) that makes the pyridinic ring more prone to
449 transfer an electron through a nucleophilic addition and consequent formation of a
450 carbamate intermediate.

451 The continuous electroreduction of CO₂ to methanol tests in a filter-press electrochemical
452 cell, showed a maximum methanol formation rate when using 2-methylpyridine (10 mM),
453 $r = 2.91 \mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ (Faradaic efficiency= 16.86%), which is significantly higher than
454 that value in the absence of any molecular catalyst, $r = 0.21 \mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ (Faradaic
455 efficiency= 1.2%). Importantly, process efficiency was significantly raised by reducing
456 the pH of the electrolyte to 5, with Faradaic efficiencies as high as $FE = 25.6\%$ for an
457 applied voltage of $E = -0.62 \text{ V vs. Ag/AgCl}$ ($j = 1 \text{ mA}\cdot\text{cm}^{-2}$) in the 2mPy (10 mM)-based
458 system. This system, however, showed deactivation at longer reaction times, which may
459 be associated to a change in the selectivity of the reaction (i.e. formation of ethylene).

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