### Electrochemistry



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# Aqueous Electrochemical Reduction of Carbon Dioxide and Carbon Monoxide into Methanol with Cobalt Phthalocyanine

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Abstract: Conversion of  $CO_2$  into valuable molecules is a field of intensive investigation with the aim of developing scalable technologies for making fuels using renewable energy sources. While electrochemical reduction into CO and formate are approaching industrial maturity, a current challenge is obtaining more reduced products like methanol. However, literature on the matter is scarce, and even more for the use of molecular catalysts. Here, we demonstrate that cobalt phthalocyanine, a well-known catalyst for the electrochemical conversion of  $CO_2$  to  $CO_2$  can also catalyze the reaction from  $CO_2$  or CO to methanol in aqueous electrolytes at ambient conditions of temperature and pressure. The studies identify formaldehyde as a key intermediate and an unexpected pH effect on selectivity. This paves the way for establishing a sequential process where  $CO_2$  is first converted to CO which is subsequently used as a reactant to produce methanol. Under ideal conditions, the reaction shows a global Faradaic efficiency of 19.5% and chemical selectivity of 7.5%.

he electrochemical reduction of carbon dioxide (CO<sub>2</sub>) into methanol (CH<sub>3</sub>OH) is considered as a major target that could enable a transition from fossil fuels to renewable fuels. To catalyze the six-electron-six-proton reduction of CO<sub>2</sub> to CH<sub>3</sub>OH, efforts have been devoted to the use of metal oxides, metal alloys, or chalcogenide-based catalytic electrodes.<sup>[1-4]</sup> Most of these materials either require the use of rare metals, or are not selective for methanol because they cogenerate more reduced products (for example, methane or C<sub>2</sub> molecules).<sup>[5,6]</sup> Additionally, the thermodynamic stability window of metal oxides is limited<sup>[7]</sup> and the reduced metal electrodes typically have low activity for CH<sub>3</sub>OH production,<sup>[8]</sup> leading to performance instability. One promising strategy to achieve high selectivity is to use molecular catalysts to precisely control the structure of the active site. Even though such a strategy has been successfully implemented for CO<sub>2</sub>-to-CO production,<sup>[9,10]</sup> no molecular catalyst has been shown to perform the reaction up to CH<sub>3</sub>OH yet. A series of reports with transition-metal complexes were published in the 80s, which, upon assistance from a heterogeneous co-catalyst (Everitt's salt) deposited on a platinum electrode, showed some methanol evolution.<sup>[11-13]</sup> A few papers have reported traces of CH<sub>3</sub>OH production when using metal complexes, including cobalt phthalocyanine (CoPc) as a catalyst, but the exact source of the alcohol was not identified<sup>[14]</sup> and no follow-up studies were published.<sup>[15,16]</sup> Here, we demonstrate for the first time that CoPc is able to electroreduce CO<sub>2</sub> into CH<sub>3</sub>OH in aqueous media through a CO intermediate. Since the CO<sub>2</sub>-to-CO step is very efficient at a neutral pH, further optimization was focused on the CO to CH<sub>3</sub>OH step. In basic media (pH 12–13), we used pure CO as a substrate and discovered experimental conditions to reach a nearly 50-fold increase for the Faradaic efficiency (FE) towards methanol generation (from 0.3 to 14.3%). Formaldehyde (HCHO) was also identified as an intermediate. Upon combination of an optimized CO2-to-CO step in a first electrolyzer and the following reduction step of pure CO to methanol in a second electrolyzer, an overall FE from CO<sub>2</sub> to CH<sub>3</sub>OH of 19.5% may be achieved.

CoPc, a well-studied catalyst in electrochemistry,<sup>[17,18]</sup> belongs to the phthalocyanine family that are used as a dve at a large scale in the painting industry. This catalyst is particularly appealing due to its low cost. Upon mixing the cobalt complex with multi-wall carbon nanotubes (MWCNT) and Nafion resin in a mixture of ethanol and ethylene glycol, a colloidal, stable ink was obtained (see Supporting Information). After ink deposition onto porous carbon paper, the material was dried at 100 °C resulting in the porous catalytic film observed from SEM (Supporting Information, Figure S1). The typical CoPc concentration in the film was about  $15.7 \pm 0.7$  nmol cm<sup>-2</sup>. Electrolyses were then conducted in aqueous solutions under a series of various pH conditions and CO<sub>2</sub> or CO atmosphere (see Table S1 for a full description). Both the liquid and the gas phases were analyzed following electrolysis by <sup>1</sup>H NMR and gas chromatography (GC), respectively. The results are summarized in Table 1 and the full set of collected data is reported in the Supporting Information (Tables S1 and S2). After 3 h of electrolysis in a CO<sub>2</sub>-saturated 0.5 M KHCO<sub>3</sub> solution (pH 7.2) at an applied potential of -0.68 V vs. RHE, no traces of CH<sub>3</sub>OH were detected. However, when decreasing the potential to -0.88 V

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	Substrate	рН	<i>E</i> [V vs. RHE]	<i>t</i> [h]	$j_{ m total}  [ m mA cm^{-2}]$	CH <sub>3</sub> OH		
						FE [%]	$j [mA cm^{-2}]$	TON
1	CO <sub>2</sub>	7.2	-0.88	3	11.25	0.3	0.03	44
2	HCOO <sup>-</sup>	7	-0.89	2	15.85	0	0	0
3	СО	7	-0.89	2	5.34	1.1	0.06	70
4	СО	7	-0.99	2	2.72	2.3	0.06	76
5	СО	13	-0.54	2	1.12	2.9	0.03	40
6	СО	13	-0.64	1.5	4.77	14.3	0.68	556
7	СО	12	-0.70	2	2.68	12.1	0.32	400
8	НСНО	13	-0.54	2	10.16	18.2	1.85	4588
9	НСНО	13	-0.64	1	25.16	11.6	2.91	3621
10	СО	14	-0.63	0.5	3.08	0.9	0.03	10
11	СО	13	-0.99	1	27.77	0	0	0
12 <sup>[a]</sup>	СО	13	-0.64	1	2.01	0	0	0
13 <sup>[b]</sup>	CO	13	-0.64	0.5	0.98	0	0	0

 Table 1:
 Electrolysis results and Faradaic efficiencies for methanol production.

 $CO_2$  and CO were used as reactant substrates upon saturation in water at 25 °C and 1 atm (leading to a concentration of 34 mm and 1 mm, respectively, at neutral pH). Concentration of HCOO<sup>-</sup> and formaldehyde were 10 and 20 mm, respectively. Except for [a] and [b], CoPc is the catalyst: ([a] catalyst: electrodeposited metallic Co), ([b] catalyst: CoQpy complex).

vs. RHE (Figure 1 a), we detected a small amount of CH<sub>3</sub>OH from the <sup>1</sup>H NMR spectra (Figure S2) of the electrolyte solution. This corresponds to a Faradaic efficiency (FE) of 0.3% and to a partial current density ( $j_{CH_3OH}$ ) of 30 µA cm<sup>-2</sup> (entry 1, Table 1). An isotopic-labelling experiment, conducted in a KH<sup>13</sup>CO<sub>3</sub> solution saturated with <sup>13</sup>CO<sub>2</sub> under the same electrochemical conditions as described above provided a clean split of the <sup>1</sup>H NMR signal which represents the CH<sub>3</sub> proton peak ( $\delta = 3.35$  ppm) into a doublet with a coupling constant ( $J_{\rm HC}$ ) of 142 Hz (Figure S3). This unambiguous signature of the <sup>13</sup>CH<sub>3</sub>OH species confirmed that <sup>13</sup>CO<sub>2</sub> is the source of the observed methanol. Since carbon monoxide (CO) and formate (HCOO<sup>-</sup>) were also detected after electrolysis under a CO<sub>2</sub> atmosphere, with FEs of 33.6% and 1.3%, respectively (entry 1, Table S2), electrolyses were performed using both compounds as substrates. At the same pH (7), electrolysis of a formate solution did not produce any traces of CH<sub>3</sub>OH (entry 2, Table 1). On the contrary, under



**Figure 1.** Current density and charge vs. time for a) a 3 h electrolysis under a CO<sub>2</sub> atmosphere (pH 7.2) at -0.88 V vs. RHE, b) a 2 h electrolysis under a CO atmosphere (pH 12) at -0.70 V vs. RHE, c) a 1 h electrolysis with 20 mM formaldehyde (under an argon atmosphere) at -0.64 V vs. RHE. d) Co K-edge XANES spectra of the starting CoPc complex (black dots) and of a CoPc-MWCNT film before (gray) and after (black) 2 h of electrolysis at E = -0.64 V vs. RHE under a CO atmosphere (pH 13).

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a CO atmosphere, CH<sub>3</sub>OH was produced with a FE of 1–2% and a partial current density  $j_{CH_3OH}$  of 0.06 mA cm<sup>-2</sup>, slightly larger than those obtained from a CO<sub>2</sub>-saturated solution (entries 3–4, Table 1). Upon raising the solution pH to 13 (entries 5–6 in Table 1), the FE for CH<sub>3</sub>OH increased to 14.3% at E = -0.64 V vs. RHE. Similarly, the partial current density for CH<sub>3</sub>OH was enhanced by a factor about 10, increasing up to 0.68 mA cm<sup>-2</sup>, while  $j_{H_2}$  remained in the same order of magnitude. Concomitantly, the overpotential decreased by 170 mV (from 910 mV to 740 mV) compared to CO<sub>2</sub> electrolysis. A labelled experiment with <sup>13</sup>CO confirmed that the carbon monoxide is the source for the methanol (Figure 2). When the pH value was further increased to 14, the activity decreased.



**Figure 2.** <sup>1</sup>H NMR spectra of the solution after controlled potential electrolysis (E = -0.64 V vs. RHE, t = 2 h) in <sup>12</sup>CO- (gray trace) and <sup>13</sup>CO-saturated (black trace) solutions at pH 13.

Following a 2 h electrolysis at -0.54 V vs. RHE and pH 13 under CO, the catholyte solution was analyzed by highpressure liquid chromatography (HPLC) after derivatization with 2,4-dinitrophenylhydrazine (DNPH) (see Supporting Information). Formaldehyde was detected and the Faradaic efficiency for its formation was 3.3%, leading to a complete FE of 87.6%. No other products than formaldehyde, methanol, and H<sub>2</sub> were detected.

Careful attention has to be paid to the Cannizzaro reaction that may spontaneously take place in alkaline media and even in neutral media in the reaction layer of the cathode where a high pH could build up.<sup>[19]</sup> This reaction, which amounts to formaldehyde disproportionation, may indeed be a source for CH<sub>3</sub>OH and HCOO<sup>-</sup> and can be misleading in product analysis since it does not involve any Faradaic process. In a blank experiment, depolymerized paraformaldehyde was used as a source for formaldehyde in a typical electrolysis solution (0.1M KOH, pH 13). The formaldehyde solution (20 mM) was then stirred for 2 h and <sup>1</sup>H NMR analysis was performed. In accordance with Cannizzaro's mechanism,<sup>[20]</sup> the ratio between the quantities of CH<sub>3</sub>OH and HCOO<sup>-</sup> is equal to 1 when the reaction occurs (Figure S4). By the end of an electrolysis in a CO-saturated solution at pH 13, the ratio between methanol and formate concentrations was equal to 16 and even to 27 at pH 12 where Cannizzaro is less favored (Figure S5 and entry 7, Table 1). Therefore, these experiments demonstrate that the Cannizzaro process can only account for a small fraction of the produced  $CH_3OH$ . This conclusion is supported by the fact that cyclic voltammetry of the catalytic film provided a higher catalytic current in the presence of formaldehyde than without (Figure 3).



**Figure 3.** Cyclic voltammetry measurements of a CoPc/MWCNT film ( $\Gamma$ (CoPc) = 15 nmol cm<sup>-2</sup>) in a 0.1  $\mu$  KOH solution under an Ar atmosphere without (gray) and with 20 m $\mu$  HCHO (black). Scan rate = 20 mVs<sup>-1</sup>, geometric electrode surface S<sub>WE</sub> = 0.30 cm<sup>2</sup>.

Also, electrolysis with dissolved formaldehyde performed in an Ar-saturated solution (Figure 1 c) gave more than 18% FE for CH<sub>3</sub>OH at a potential of -0.54 V vs. RHE, which corresponds to 770 mV overpotential (entry 8, Table 1). At a slightly more negative electrolysis potential (-0.64 V vs. RHE), a maximum partial current density of 2.91 mA cm<sup>-2</sup> was reached (entry 9, Table 1). In order to properly evaluate both  $j_{CH_3OH}$  and FE<sub>CH<sub>3</sub>OH</sub> values reported in Table 1, the formate production was carefully quantified after each electrolysis and subtracted from the total amount of CH<sub>3</sub>OH as summarized in Equation (1).

$$n_{\rm CH_3OH,Faradaic} = n_{\rm CH_3OH,total} - n_{\rm CH_3OH,Cannizzaro}$$

 $= n_{\rm CH_3OH,total} - n_{\rm HCOO-,total}$ 

(1)

It should be noted that this calculation does not apply for experiments under  $CO_2$ -saturation conditions since it is not possible to distinguish the portion of  $HCOO^-$  originating from the Faradaic reduction of  $CO_2$  and the portion ascribed to the homogeneous Cannizzaro process. Therefore, a fraction of the CH<sub>3</sub>OH reported in entry 1 of Table 1 could come from the Cannizzaro process rather than from a Faradaic reduction of  $CO_2$ , but it should be even smaller than in the above experiments since the Cannizzaro reaction rate is slow at a pH of 7.2.

Identification of formaldehyde as an intermediate provides a rational explanation for the decay of  $j_{CH_3OH}$  under CO

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atmosphere when the pH was raised from 13 to 14 (see entries 6 and 10 in Table 1). Indeed, methylene glycol (the aqueous form of formaldehyde) has a  $pK_a$  of about  $13^{[21]}$  and is mostly deprotonated at pH 14. This is supported by a similar drop in methanol production (< 3% FE) when starting with formaldehyde as a substrate at pH 14. Interestingly, when methanol itself was used as a starting substrate (20 mm, controlled potential electrolysis at -0.64 V vs. RHE and pH 13 for 2 h), no traces of other products such as methane were detected from GC analysis of the headspace, further illustrating the selectivity of the catalysis towards CH<sub>3</sub>OH formation.

To assess the molecular nature of the catalysis and examine the possibility that the observed reactivity is due to decomposition of CoPc into metallic Co nanoparticles,<sup>[22]</sup> a series of control experiments were performed with various films in CO-saturated solutions at pH 13. The first film was prepared by replacing CoPc with an electrodeposited CoCl<sub>2</sub> film with an equivalent amount of Co atoms. The second film was obtained by replacing CoPc with an identical concentration of cobalt quaterpyridine (CoQpy), a more fragile catalyst<sup>[23]</sup> that demetalates at negative potentials. Finally, a third film was made with CoPc, but was subjected to a more negative potential (E = -0.99 V vs. RHE) to accelerate catalyst decomposition. In all these experiments, no CH<sub>3</sub>OH was found in the catholyte after electrolysis, indicating that the aforementioned catalysis of CO<sub>2</sub> to CH<sub>3</sub>OH is indeed a molecular-driven process. This is also supported by the fact that an anodic scan of the catalytic film right after electrolysis failed to detect any oxidative stripping peak that would correspond to the oxidation of electrodeposited metallic Co (Figure S6). The Co K-edge X-ray absorption near-edge structure (XANES) spectra of the CoPc starting complex as well as the CoPc-MWCNT electrodes before and after electrolysis at -0.64 V vs. RHE under CO atmosphere are shown in Figure 1d. The three spectra present the typical features expected for cobalt phthalocyanine complexes: a first, low-intensity pre-edge peak at 7710 eV which is assigned to the  $1s \rightarrow 3d/4p$  transition and a second intense peak at 7716 eV for the  $1s \rightarrow 4p_z$  transition which is characteristic to Co-N4 interactions.<sup>[24,25]</sup> Only slight changes are observed after catalysis, which can be attributed to changes in the interactions between CoPc and the MWCNTs.<sup>[24]</sup> A comparison of the spectrum obtained after electrolysis with those of reference cobalt species further demonstrates the intactness of the CoPc-MWCNT hybrid (Figure S7). However, it should be noted that the catalytic activity progressively decreased at longer times, as observed from the drop of the Faradaic yield for methanol production after a couple of hours. It may be due to reductive hydrogenation of the C=N double bonds of the phthalocyanine core, which has already been previously reported.<sup>[26]</sup> The exact mechanism of deactivation is under active study but we already know that basic media is not detrimental since a similar cobalt phthalocyanine has recently been shown to be stable for more than 10 h under strongly alkaline conditions (pH 14) for the CO<sub>2</sub>-to-CO step at a gas diffusion electrode.<sup>[27]</sup> Because of the rather fast deactivation and variation in formaldehyde concentration over time (the ratio between electrode surface and electrolyte volume affects the formaldehyde concentration and thus its reaction rate), the typical uncertainty is in the range of 10-20%.

All previous results converge to a simple sequential strategy for optimizing methanol production. CoPc can first efficiently catalyze the electrochemical CO<sub>2</sub>-to-CO conversion with a high FE (95%) in a flow cell with current densities up to 150 mA cm<sup>-2</sup> as we recently demonstrated.<sup>[28]</sup> Pure CO can then be used as a reactant under basic conditions (pH 13) and be reduced to CH<sub>3</sub>OH with 14.3% efficiency (740 mV overpotential). The catalyst is the same for each step, while the pH and the electrode potential are adjusted to maximize each partial reduction process. From the total number of transferred electrons, a global Faradaic efficiency of 19.5% is calculated and the chemical selectivity is about 7.5% (Figure S8).

In summary, cobalt phthalocyanine was used as a catalyst for the electrochemical conversion of CO<sub>2</sub> to methanol, thanks to the unlocking of the CO-to-methanol step. The simplicity of the catalyst, the facile procedure for preparing the catalytic electrode, and the low loading amounts of the catalyst make the process versatile and easy to implement. Beyond this proof of principle, a tuning of the ligand will rapidly lead to improved performances and will be guided by mechanistic studies that are currently being done in our laboratories. We have thus shown that the electrochemical multi-electron-multi-proton reduction of CO<sub>2</sub> beyond CO and formate can be achieved and controlled with a molecular catalyst. This study illuminates a new field of research for employing earth-abundant metal-based molecular complexes bearing simple ligand structures as cascade electrocatalysts for liquid-fuel production from CO2 and renewable electricity in mild aqueous conditions.

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#### Conflict of interest

The authors declare no conflict of interest.

Keywords: carbon-monoxide reduction · cobalt phthalocyanine · electrochemistry · methanol · molecular catalyst

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## **Communications**



Aqueous Electrochemical Reduction of Carbon Dioxide and Carbon Monoxide into Methanol with Cobalt Phthalocyanine



**Turning the wheel even further**: Cobalt phthalocyanine, a well-known catalyst for the electrochemical reduction of  $CO_2$  to CO, is reported to further reduce carbon monoxide into methanol in aqueous electrolytes at ambient conditions of temperature and pressure. Formaldehyde is an intermediate on the reaction pathway. Under optimized conditions,  $CO_2$ can be converted into methanol in two electrochemical steps with a 19.5% global Faradaic efficiency.

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