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## Electrocatalytic reduction of CO<sub>2</sub> and nitrate on immobilized metal porphyrins

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# Chapter 2

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## **Electrocatalytic reduction of carbon dioxide to carbon monoxide and methane at an immobilized cobalt protoporphyrin in aqueous solution**

### **ABSTRACT**

In this Chapter we report that a cobalt protoporphyrin immobilized on a pyrolytic graphite electrode is able to reduce carbon dioxide in acidic solution at relatively low overpotential ( $-0.5$  V), with an efficiency and selectivity that is comparable to the best porphyrin-based electrocatalyst in the literature. Whilst carbon monoxide is the main reduction product, we also observe methane (and smaller amounts of formic acid and methanol) as by-product. We find that an unbuffered solution of  $\text{pH}=3$  is most advantageous for selective carbon dioxide reduction. Our results are explained consistently by a mechanism in which carbon dioxide is activated by the cobalt-protoporphyrin through the stabilization of a anion intermediate, which acts as Brønsted base. The basic character of this intermediate explains how the carbon dioxide reduction circumvents a mechanism in which concerted proton-electron transfer takes place, in contrast to the hydrogen evolution mechanism. Our results and their mechanistic interpretations suggest strategies for designing improved catalysts.

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## 2.1. Introduction

The efficient electrochemical reduction of carbon dioxide to a fuel with a high-energy density would be a major step forward in the introduction of a CO<sub>2</sub>-neutral energy cycle, as it would allow for the direct low-temperature conversion of photo-generated electrical current to stored chemical energy, in a fashion very similar to the way nature stores solar energy. Plants fix CO<sub>2</sub> from the atmosphere by photosynthesis, in an enzymatic complex called Rubisco, which selectively binds CO<sub>2</sub> and inserts it into existing carbon chains by reductive carboxylation. The high-energy electrons necessary for this process are photo-generated by Photosystem II.

Synthetic catalysts for the electrocatalytic reduction of CO<sub>2</sub>, which could facilitate such an artificial CO<sub>2</sub> neutral redox cycle, have been studied for many decades<sup>1-4</sup>. A main challenge in electrochemical CO<sub>2</sub> reduction is to develop catalysts that are capable of reducing CO<sub>2</sub> beyond the two-electron products carbon monoxide (CO), formic acid (HCOOH), and oxalate (C<sub>2</sub>O<sub>4</sub><sup>2-</sup>). Unfortunately, the formation of reduction products requiring 4 or more electrons is invariably associated with considerable overpotentials due to the multiple intermediates involved in the reaction mechanisms<sup>5</sup> (although more reduced products often have higher stability and correspondingly more positive equilibrium potentials). Metallic copper is unique in producing significant amounts of high-energy multi-electron transfer products such as methane, ethylene and ethanol<sup>3,6,7</sup>. Molecular catalysts capable of reducing CO<sub>2</sub> to a product different from one of the abovementioned two-electron products, are much less common and typically involve a strong interaction with the working electrode<sup>8</sup>. A second important challenge in CO<sub>2</sub> electrocatalysis concerns the suppression of the concomitant evolution of hydrogen, which is a dominant side reaction for CO<sub>2</sub> reduction from aqueous electrolytes. Strategies for suppressing hydrogen evolution typically involve working with high(er) CO<sub>2</sub> to proton ratios, such as high CO<sub>2</sub> pressures or solvents with a higher CO<sub>2</sub> solubility.

Recent fundamental and theoretical work has reconsidered porphyrin-based molecular catalysts for electrochemical CO<sub>2</sub> reduction. Tripkovic et al. have performed extensive

density functional theory calculations of metal-functionalized porphyrin-like graphene surfaces and predicted the potential formation of methane and methanol from  $\text{CO}_2$ <sup>9</sup>. Costentin et al. considered ligand modifications of iron-based porphyrins and found that local proton sources built into the porphyrin ring give rise to high activity and good Faradaic efficiency for the reduction of  $\text{CO}_2$  to CO in a mixed DMF-water solvent<sup>10</sup>. In fact, it has been known since the early 1980s that cobalt-based macrocyclic complexes, either in solution or adsorbed onto carbon electrodes, act as effective electrocatalysts for  $\text{CO}_2$  reduction, producing CO, formic acid, methanol and methane, though at relatively high overpotential and with varying selectivity<sup>11-15</sup>.

In this Chapter, we report on the electrochemical reduction of  $\text{CO}_2$  to CO and methane, as well as smaller amounts of formic acid and methanol, on a simple cobalt-protoporphyrin molecular catalyst immobilized onto a pyrolytic graphite electrode in a purely aqueous electrolyte solution. Previous similar work employing immobilized cobalt-porphyrins or cobalt-phthalocyanines has shown the capability of Co-based catalysts to achieve a high Faradaic efficiency towards CO, which is highly sensitive to pH and potential<sup>16-18</sup>. Our work confirms that immobilized cobalt-based porphyrins are good  $\text{CO}_2$  reduction electrocatalysts capable of producing multi-electron products such as methane and methanol. More significantly, our work underscores the important role of pH in steering the catalytic activity and selectivity toward CO and  $\text{CH}_4$ , especially in the very narrow pH=1-3 range in the absence of coordinating anions. This high sensitivity to pH is explained by a mechanism highlighting the important role of the initial electron transfer in activating  $\text{CO}_2$  electrochemically. For the first time we demonstrate how such a mechanism for  $\text{CO}_2$  reduction manifests experimentally and how this property can be exploited to suppress concomitant hydrogen evolution. Furthermore, we show that the overpotential and corresponding turnover frequency for  $\text{CO}_2$  reduction of our catalyst compare favorably to the best molecular porphyrin-based catalyst in the literature<sup>10</sup>. Therefore, we believe that these insights have significant implications for the design of new and improved molecular catalyst electrodes and for the formulation of optimized process conditions for efficient electrochemical  $\text{CO}_2$  reduction to CO as well as to products reduced to a more significant degree.

## 2.2. Experimental

### 2.2.1. *Electrochemistry and chemicals*

The experiments were performed on home-made pyrolytic graphite electrodes (Carbone-Lorraine; diameter, 5mm). Before each experiment, the electrodes were polished using P500 and P1000 SiC sandpaper consecutively, and ultrasonicated in ultrapure water (MilliQ gradient A10 system, 18.2 M $\Omega$  cm) for 1 min and dried in a flow originating from compressed air. The electrodes were subsequently immersed in the cobalt protoporphyrin (CoPP, Frontier Scientific) solution (0.5 mM in borate buffer) for 5 min to immobilize the protoporphyrin on the surface and rinsed with ultrapure water prior to the experiments. A one-compartment electrochemical cell was used, with a platinum flag as counter electrode and a reversible hydrogen electrode (RHE) as a reference, to which all potentials in this work are referred. The reference electrode was separated from the working electrode compartment through a Luggin capillary. An Ivium potentiostat/galvanostat (IviumStat) was used for the electrochemical measurements. Solutions were prepared from HClO<sub>4</sub> (Merck, 70%), NaClO<sub>4</sub> (Sigma-Aldrich,  $\geq$  98.0%), NaOH (Sigma-Aldrich, 99.998%), Borate (Sigma-Aldrich) and ultrapure water. Argon (Hoekloos, purity grade 6.0) was purged through the solutions for 30 min before the experiment to remove dissolved oxygen. The reported current densities refer to the geometric surface area.

### 2.2.2. *Online electrochemical mass spectrometry*

The volatile products of the CO<sub>2</sub> electrochemical reduction were detected using on-line electrochemical mass spectrometry (OLEMS) with an Evolution mass spectrometer system (European Spectrometry systems Ltd)<sup>19</sup>. A porous Teflon tip (inner diameter, 0.5mm) with a pore size of 10-14  $\mu$ m was positioned close ( $\sim$ 10  $\mu$ m) to the center of the electrode. Prior the experiments, the tip was dipped into a 0.2 M K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in 2 M H<sub>2</sub>SO<sub>4</sub> solution for 15 min and rinsed with ultrapure water thoroughly. The gas products were collected through a PEEK capillary into the mass spectrometer. A 2400V SEM voltage was applied for all the fragments except for hydrogen (m/z=2) which is 1500 V. The OLEMS measurement was

conducted while cyclic voltammetry was scanning from 0 V to -1.5 V and back at a scan rate of 1 mV s<sup>-1</sup>.

### ***2.2.3. Gas Chromatography***

The quantitative measurements of the gas products were carried out using Gas Chromatography (GC)<sup>20,21</sup>. At atmospheric pressure, CO<sub>2</sub> was continuously purged through a two-compartment flow cell with a volume of 12 mL for each compartment at a rate of 5 mL/min for 30 min to saturate the electrolyte. The flow rate declined to 2 mL/min while a constant potential was applied for 1h. The reference electrode used here is a Ag/AgCl electrode. The experiments at high CO<sub>2</sub> pressure (P=10 atm) were conducted in a stainless-steel autoclave using a Pt mesh as a counter electrode, and a home-made Ag/AgCl in 3 M KCl as a reference electrode. All potentials were scaled to RHE after the experiments for both atmospheric and high pressure, with  $E \text{ (vs Ag/AgCl)} = E \text{ (vs RHE)} - 0.197 \text{ V} - \text{pH} \times 0.059$ . CO<sub>2</sub> was continuously purged through the autoclave before and during the electrolysis with a flow rate of 50 mL min<sup>-1</sup>. The reactor effluent was sampled via GC once every 6 min. CO, CO<sub>2</sub>, H<sub>2</sub> and hydrocarbons were simultaneously separated using two series columns in series (a ShinCarbon 2 m micropacked column and a Rtx-1 column). The quantitative analysis of the gas products was performed using a thermal conductivity detector (H<sub>2</sub> and CO) and flame ionization detector (hydrocarbons).

### ***2.2.4. Online High Performance Liquid Chromatography***

High-performance liquid chromatography (HPLC, Prominence HPLC, Shimadzu) was used to detect liquid products produced during electrochemical reduction of CO<sub>2</sub> using a method described in previous work<sup>22</sup>. Samples were collected using a Teflon tip (inner diameter: 0.38 mm) positioned ~10 μm from the center of the electrode surface (diameter: 1 cm). The sample volume collected was 60 μL stored in a 96-well microtiter plate (270 μL per well, Screening Device b.v.) using an automatic fraction collector (FRC-10A, Shimadzu). The flow rate of the sample collection was adjusted to 60 μL per min with a Shimadzu pump (LC-20AT). A linear sweep voltammogram was recorded while the sample was collecting at a scan rate of 1 mV s<sup>-1</sup> from 0 V to -1.5 V vs RHE. The microtiter plate with collected

samples was then placed in an auto-sampler (SIL-20A) holder and 30  $\mu\text{L}$  of sample was injected into an Aminex HPX 87-H (Bio-Rad) column. The eluent was diluted sulfuric acid (5 mM) with a flow rate of 0.6 mL per min. The temperature of column was maintained at 85°C using a column oven (CTO-20A) and the separated compounds were detected with a refractive index detector (RID-10A).

## 2.3. Results

### 2.3.1. Voltammetry and online electrochemical mass spectrometry

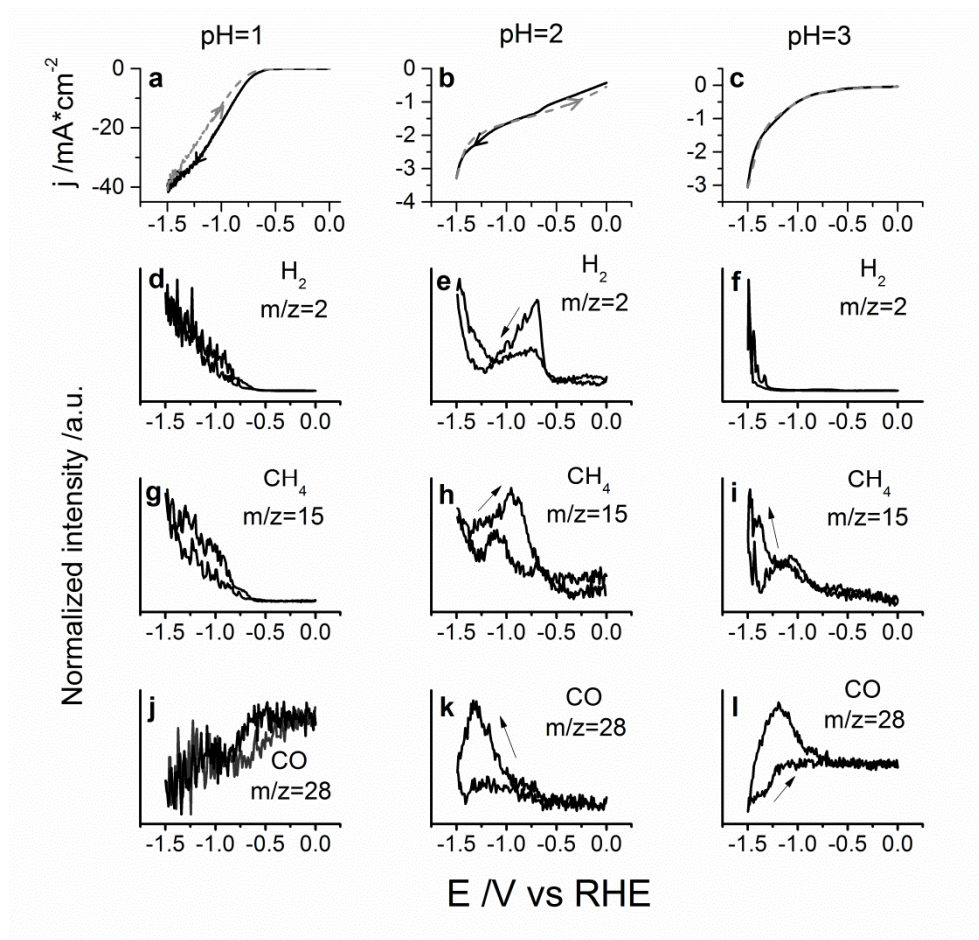
The cobalt protoporphyrin coated pyrolytic graphite (“CoPP-PG”) electrode was prepared following a procedure described earlier<sup>23</sup> and detailed in the Methods section. In situ electrochemical scanning tunneling microscopy and atomic force microscopy images of iron and zinc protoporphyrins on basal plane graphite electrodes by Tao et al. suggest that these molecules form monolayer films on the electrode with the molecules lying flat<sup>24</sup>. The blank cyclic voltammograms of the PG electrode, the CoPP-PG electrode in 0.1 M  $\text{HClO}_4$ , and the voltammetry of the dissolved CoPP in the same electrolyte, are compared in Appendix A Figure 1. The voltammetry in Appendix A Figure 1 shows the reversible redox peak of the  $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$  transition at 0.8-0.85 V vs. RHE, from which the coverage of the CoPP on the PG electrode can be determined to be ca.  $4 \times 10^{-10}$  mol  $\text{cm}^{-2}$ , in good agreement with previous experiments of protoporphyrins on pyrolytic graphite<sup>23,25</sup>. No further redox transition of the CoPP is observed at more negative potential, with the onset of hydrogen evolution being at ca. -0.5 V vs. RHE. However, we note that we have previously observed a  $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$  transition at ca. -0.6 V vs. NHE for CoPP immobilized in a DDAB (didodecyl dimethylammonium bromide) film on PG<sup>23</sup>. The observation of this peak in the DDAB films may be related to the higher hydrophobicity of DDAB. The  $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$  redox transition has previously been associated with the onset of electrocatalytic hydrogen evolution on Co porphyrins<sup>26</sup>.

Figure 1 shows the voltammetry at 1  $\text{mV s}^{-1}$  of the CoPP-PG electrode in unbuffered 0.1 M perchlorate solution of pH=1, 2 and 3, saturated with  $\text{CO}_2$ , together with the mass

signals corresponding to  $\text{H}_2$  ( $m/z=2$ ),  $\text{CH}_4$  ( $m/z=15$ , corresponding to the  $\text{CH}_3$  fragment) and  $\text{CO}$  ( $m/z=28$ ) as measured simultaneously using online electrochemical mass spectrometry (OLEMS)<sup>27</sup>. The OLEMS experiment samples the gases formed at the electrode surface by a tip covered with a hydrophobic membrane placed at a distance of ca. 10  $\mu\text{m}$  from the surface. This technique can follow gas production online during cyclic voltammetry. Calibration of our experiment is cumbersome as the signals depend on parameters which are not easy to control (tip distance, tip porosity). Quantitative measurements were therefore performed using long-term electrolysis combined with gas chromatography (to be discussed later). Depending on the quality of the gas-sensing tip used in the OLEMS experiment shown in Fig.1,  $m/z=31$  was also measured, corresponding to the formation of methanol (see Appendix A Figure 2). Using HPLC, we could also detect formic acid as one of the products (see Appendix A Figure 3), though both formic acid and methanol appear to be minority products under these conditions. This confirms, for the first time in a single study, that all four products,  $\text{CO}$ ,  $\text{HCOOH}$ ,  $\text{CH}_3\text{OH}$ , and  $\text{CH}_4$  can be formed from  $\text{CO}_2$  reduction on a Co-based porphyrin. Fig. 1(a, d, g) measured at  $\text{pH}=1$ , shows that the reduction current is accompanied by the simultaneous formation of  $\text{H}_2$  and  $\text{CH}_4$ . The  $m/z=28$  signal in Figure 1 was not corrected for the  $\text{CO}_2$  fragmentation, and therefore the  $\text{CO}$  signal combines  $\text{CO}$  production from  $\text{CO}_2$  electroreduction with  $\text{CO}$  formation from  $\text{CO}_2$  fragmentation in the MS. This explains why the  $\text{CO}$  signal decreases for more negative potentials at which the  $\text{CO}_2$  reduction rate is higher, as a result of the lower local  $\text{CO}_2$  concentration near the electrode surface. However, at  $\text{pH}=2$  and 3, an increase in the  $\text{CO}$  signal with more negative potential is observed, simultaneously with the  $\text{CH}_4$  production, suggesting that  $\text{CO}$  is an intermediate in the reaction (as also suggested by the fact that  $\text{CO}$  may be reduced to  $\text{CH}_4$  on CoPP-PG; see Figure 4 below). Most significantly, at  $\text{pH}=3$ ,  $\text{CO}$  and  $\text{CH}_4$  production is observed at less negative potentials than  $\text{H}_2$  evolution, showing that the  $\text{CO}_2$  reduction has a different  $\text{pH}$  dependence from the hydrogen evolution reaction. We chose to restrict ourselves to  $\text{pH} \leq 3$  in perchlorate solution in order to avoid the interference of buffering anions such as bicarbonate or phosphate (see below) with the  $\text{CO}_2$  reduction process.

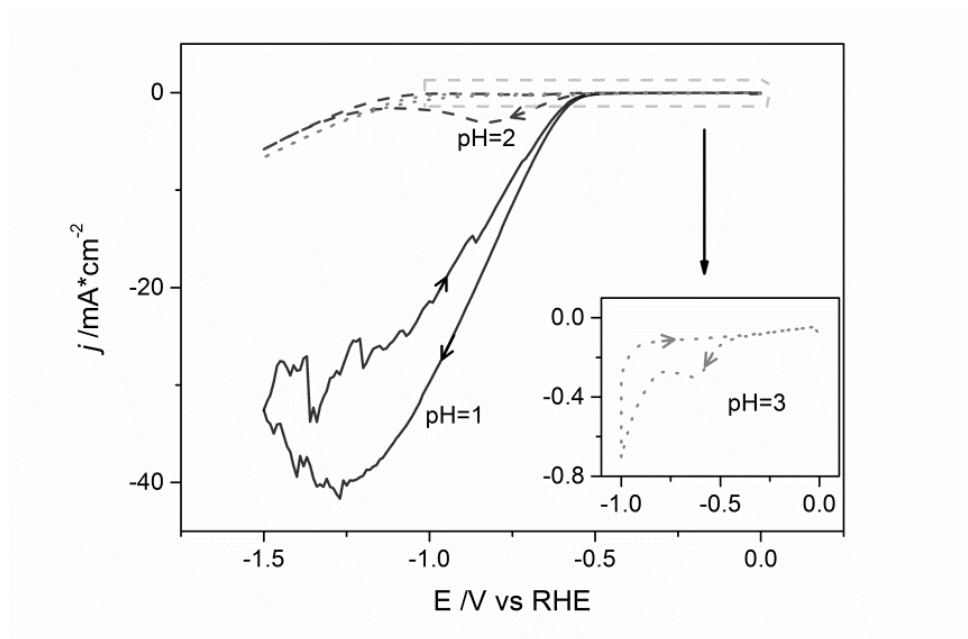
We have performed a number of experiments to convince ourselves that the Co-PP is indeed the active catalytic center turning over dissolved  $\text{CO}_2$ . On the unmodified PG electrode and on a PG electrode modified with Co-free protoporphyrin,  $\text{H}_2$  evolution was observed, but no  $\text{CO}_2$  reduction (Appendix A Figures 5 and 6). A PG electrode onto which a small amount of Co was electrodeposited was also tested for  $\text{CO}_2$  reduction, but showed no activity (Appendix A Figure 7). Finally, the reduction of isotopically labeled  $^{13}\text{CO}_2$  in deuterated water yielded  $m/z=19$  (corresponding to  $^{13}\text{CD}_3$ ) as reduction product (Appendix A Figure 8), which irrefutably proves the reduction of dissolved  $\text{CO}_2$  into methane. These combined results show that the immobilized Co-protoporphyrin is responsible for the production of carbon monoxide and methane from  $\text{CO}_2$  electroreduction.

As mentioned, the most important conclusion from Figure 1 is the remarkable role of the pH. Initially, we performed the  $\text{CO}_2$  reduction experiments at pH=2 and 3 in buffered phosphate solution, also yielding methane as a product but with a pH dependence that was not straightforward to understand. Therefore, we decided to remove the buffering phosphate anions, as they are suspected to interfere with the reactivity by coordinating to the catalytic center<sup>28</sup> or interacting with the catalytic intermediates. In non-adsorbing perchlorate solution, the role of the proton concentration can be better understood by comparing the voltammetry of the CoPP-PG in the absence of  $\text{CO}_2$  at pH=1, 2, and 3, as shown in Figure 2. At pH=1, there is only a single catalytic reduction wave in the potential window studied, corresponding to the reduction of  $\text{H}^+$  to  $\text{H}_2$ . The voltammetry at pH=2 and 3 shows two waves, one at less negative potential that is proportional to the  $\text{H}^+$  concentration and corresponds to  $\text{H}^+$  reduction, and one starting at -1.1 V that corresponds to  $\text{H}_2\text{O}$  reduction. This is also reflected in the  $\text{H}_2$  formation profiles observed in the mass signals in Figure 1. We must also take into account here that because of the relatively low proton concentration at pH=3, the direct proton reduction quickly runs into diffusion limitations, and further  $\text{H}_2$  evolution can only take place at more negative potentials by direct water reduction, which



**Figure 1 | Voltammetry and volatile product identification by online electrochemical mass spectrometry (OLEMS).** This figure shows the electrochemical reduction of CO<sub>2</sub> on cobalt protoporphyrin immobilized on a pyrolytic graphite electrode and the various volatile products detected by OLEMS. (a) Cyclic voltammetry (CV) in 0.1 M HClO<sub>4</sub>, (b) CV in 10 mM HClO<sub>4</sub> + 90 mM NaClO<sub>4</sub>, (c) CV in 1 mM HClO<sub>4</sub> + 99mM NaClO<sub>4</sub>, (d) m/z=2 (H<sub>2</sub>) signal in 0.1 M HClO<sub>4</sub>, (e) m/z=2 (H<sub>2</sub>) signal in 10 mM HClO<sub>4</sub> + 90 mM NaClO<sub>4</sub>, (f) m/z=2 (H<sub>2</sub>) signal in 1 mM HClO<sub>4</sub> + 99mM NaClO<sub>4</sub>, (g) m/z=15 (CH<sub>4</sub>) signal in 0.1 M HClO<sub>4</sub>, (h) m/z=15 (CH<sub>4</sub>) signal in 10 mM HClO<sub>4</sub> + 90 mM NaClO<sub>4</sub>, (i) m/z=15 (CH<sub>4</sub>) signal in 1 mM HClO<sub>4</sub> + 99mM NaClO<sub>4</sub>, (j) m/z=28 (CO) signal in 0.1 M HClO<sub>4</sub>, (k) m/z=28 (CO) signal in 10 mM HClO<sub>4</sub> + 90 Mm NaClO<sub>4</sub>, (l) m/z=28 (CO) signal in 1 mM HClO<sub>4</sub> + 99mM NaClO<sub>4</sub>. Blank plots, forward scans; Gray plots, back scans in (a), (b) and (c). Scan rate was 1 mV s<sup>-1</sup> in all cases. Appendix A Figure 4 shows the same data with the unnormalized MS signals as well as the signals obtained in the first and second CV scan.

does not suffer from such diffusion limitations. By comparing the results in Figure 1 and 2, we conclude that  $H_2$  evolution dominates over  $CO_2$  reduction in the presence of a high concentration of protons in solution, whereas the opposite is the case for  $pH=3$ . The activation of  $CO_2$  is apparently less sensitive to the presence of protons, implying that water molecules are just as powerful in hydrogenating the activated  $CO_2$ . This remarkable pH dependence is somewhat similar to observations made by Noda et al. during  $CO_2$  reduction on a gold electrode<sup>28</sup>. The important new finding here is that this small pH shift is the key to favoring  $CO_2$  reduction over  $H_2$  evolution, also on our molecular catalyst, especially in the absence of buffering anions. This is also evidenced by the Faradaic efficiency measurements summarized in Figure 3, to be discussed next. A mechanistic explanation for this pH sensitivity will be given at the end of this section.

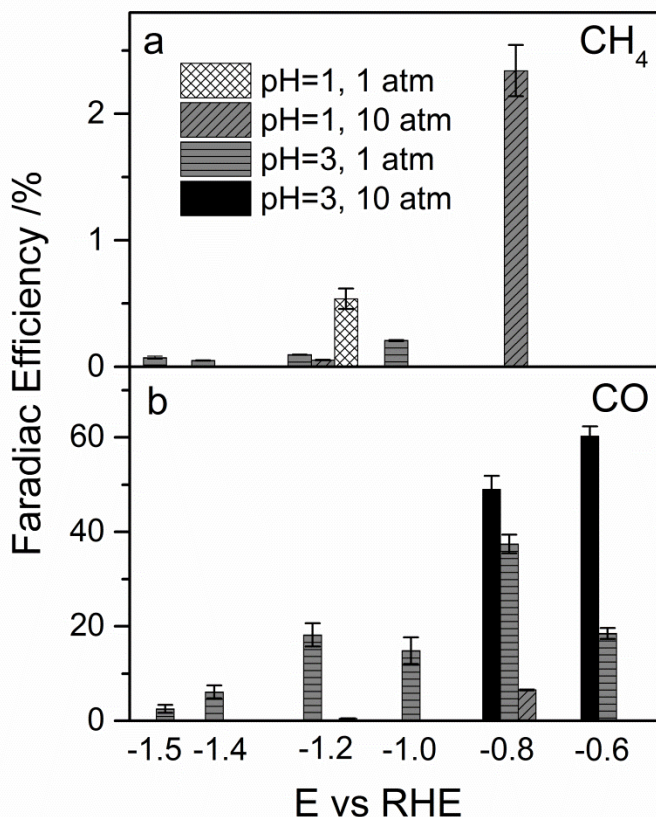


**Figure 2. pH dependence of hydrogen evolution reaction on the CoPP-PG electrode.** Hydrogen evolution reaction at  $pH=1$  (black curve),  $pH=2$  (dark gray dash curve) and  $pH=3$  (gray dot curve) on Cobalt protoporphyrin modified PG electrode in the absence of  $CO_2$ . Inserted: highlight of the voltammetry at  $pH=3$ . Scan rate was  $100 \text{ mV s}^{-1}$  in all cases. All electrolyte solutions were  $0.1 \text{ M}$  perchlorate, with different ratios of  $H^+$  and  $Na^+$ .

### 2.3.2. Faradaic efficiency

The Faradaic efficiency (FE) for the simultaneous CO<sub>2</sub> and water reduction to hydrogen, carbon monoxide and methane was determined separately with long-term electrolysis experiments, using a gas chromatography setup coupled to an electrochemical cell, as detailed elsewhere<sup>20,21</sup>. Figure 3 shows results for CO and CH<sub>4</sub> at pH =1 and 3 for different potentials. The remaining current is used to form H<sub>2</sub>. The quantitative data and error bars are summarized and further explained in Appendix A Table 1. Formic acid was also observed as a minority product at pH=1 using High Performance Liquid Chromatography, but was not observed at pH=3 (see Appendix A Figure 3). As mentioned above, methanol was observed as a product using OLEMS (Appendix A Figure 2), but it remained below the detection limit during the GC measurements. At pH=1, the Faradaic efficiency to CO and methane is low, on the order of a percent, and the dominant product is H<sub>2</sub>, and therefore for pH=1 we show results at only a single potential in Figure 3. Note however that at pH=1, more methane is produced than CO. At pH=3, a dramatic change in selectivity is observed, with now CO being a majority product, especially at less cathodic potentials, for which the Faradaic efficiency to CO is around 40%. This high selectivity is maintained for at least one hour during the long-term electrolysis experiment at fixed potential (see Appendix A Figure 9), testifying to the good stability of the catalyst. The stability and integrity of the CoPP-PG electrode was also confirmed by pre- and post-electrolysis analysis using XPS, Raman and NMR (Appendix A Figures 10-12). Raman spectroscopy showed no significant change in the spectral features of the CoPP-PG surface; XPS showed no change in Co oxidation state after 1 hour of electrolysis; and NMR showed no decomposition products in solution that could be related to CoPP. Figure 3 also illustrates that less methane is produced at pH=3 as compared to pH=1. We ascribe this lower methane production to the slower reduction of CO to CH<sub>4</sub> at pH=3 compared to pH=1 (see next paragraph). The efficiency towards CO can be further boosted by performing the experiment at higher CO<sub>2</sub> pressure. Figure 3 illustrates this for a CO<sub>2</sub> pressure of 10 atm, which leads to a Faradaic efficiency of ~ 60% at pH=3 at a potential of -0.6 V. Note that at pH=1, both the efficiency towards CO and CH<sub>4</sub> increase to a few % when the reduction is carried out at increased CO<sub>2</sub> pressure. We emphasize that OLEMS

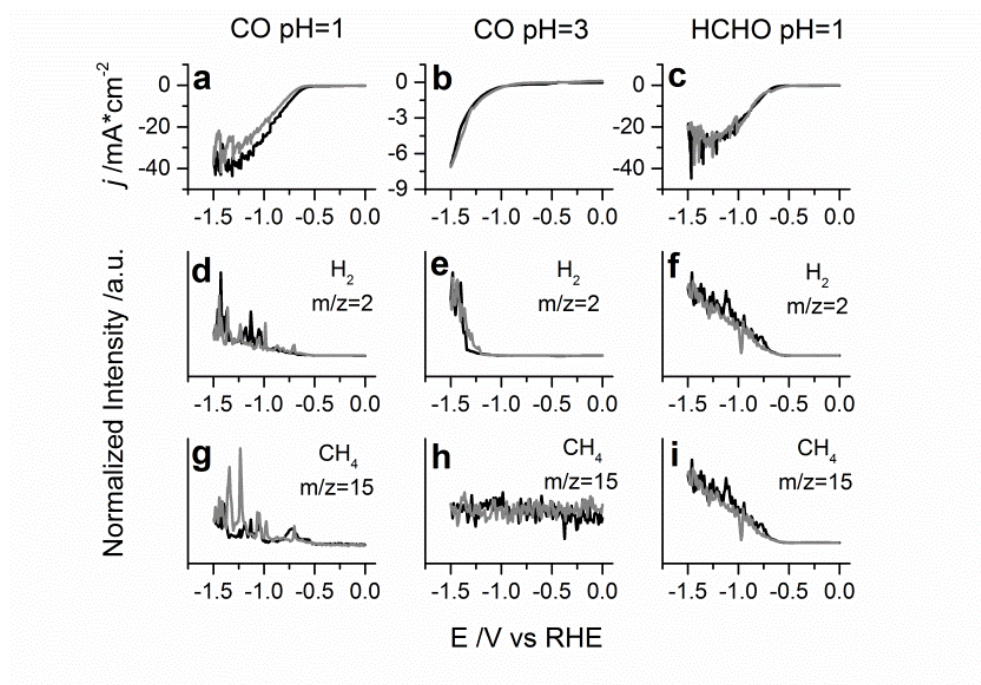
and GC experiments exhibited good consistency and reproducibility. The error bars shown in Figure 3 were based on single long-term electrolysis experiments sampled every six minutes.



**Figure 2 Faradaic efficiency of carbon dioxide reduction to carbon monoxide and methane.** Faradaic efficiencies to CO and CH<sub>4</sub> were determined for  bars: pH=1, P<sub>CO2</sub>=1 atm;  bars: pH=1, P<sub>CO2</sub>=10 atm;  bars: pH=3, P<sub>CO2</sub>=1 atm and  bars pH=3, P<sub>CO2</sub>=10 atm. Faradaic efficiency of (a) CH<sub>4</sub> and (b) CO in 0.1 M perchlorate solution saturated with CO<sub>2</sub>. At each potential the electrolysis was conducted for 1 hour at P<sub>CO2</sub>=1 atm, while it is 90 minutes at P<sub>CO2</sub>=10 atm due to the longer time to reach the steady state. Error bars were determined from 3-8 data points based on samples taken every five minutes during the steady state of a single electrolysis run.

### ***2.3.3. Reduction of CO, formic acid and formaldehyde***

To determine the involvement of potential intermediates, we also studied the reduction of formic acid (HCOOH), carbon monoxide (CO) and formaldehyde (HCHO), by combined voltammetry-OLEMS. Formic acid was not reduced at either pH=1 or 3 (Appendix A Figure 13) and is therefore an end product, not an intermediate. Figure 4 shows the voltammetry and associated OLEMS mass signals on the CoPP-PG electrode for CO reduction at pH=1 and 3 and for HCHO reduction at pH=1. Remarkably, CO is clearly reduced to methane at pH=1, simultaneous with H<sub>2</sub> evolution, but the CO reduction activity is much lower compared to hydrogen evolution at pH=3, with an insignificant amount of CH<sub>4</sub> detected. This observation is consistent with the results in Figure 3 showing that methane production from CO<sub>2</sub> is lower at pH=3. HCHO is reduced to methane at pH=1 and 3 (Figure 4 only shows pH=1). Interestingly, formaldehyde is not reduced to significant amounts of methanol, whereas methanol is the product of formaldehyde reduction on copper electrodes<sup>6</sup>. Figure 4 suggests that carbon monoxide and formaldehyde, or their catalyst-bound derivatives, are intermediates in the reaction mechanism from CO<sub>2</sub> to CH<sub>4</sub>, but formic acid is not. It also shows that the reduction of CO exhibits a different pH dependence compared to CO<sub>2</sub> reduction, explaining why the selectivity of CO<sub>2</sub> towards CO increases with higher pH, but the selectivity towards CH<sub>4</sub> decreases with higher pH.



**Figure 4 Identification of volatile products by OLEMS during electrochemical reduction of CO and HCHO.**

Cyclic voltammetry of CO reduction in (a) 100 mM  $\text{HClO}_4$  and (b) 1mM  $\text{HClO}_4$  + 99 mM  $\text{NaClO}_4$  saturated with CO with associated mass fragments of volatile products detected with OLEMS. (c) Cyclic voltammetry of HCHO (5 mM) reduction in 100 mM  $\text{HClO}_4$  with associated mass fragments measured with OLEMS. Black plots, forward scans; gray plots, backward scans. Scan rate:  $1 \text{ mVs}^{-1}$ . Appendix A Figure 14 shows the same data with the unnormalized MS signals as well as the signals obtained in the first and second CV scan.

## 2.4. Discussion

The results presented above give unique new insights into the mechanism of  $\text{CO}_2$  electroreduction on immobilized Co-protoporphyrins, and the observed pH dependence reveals the important role of the initial electron transfer to  $\text{CO}_2$  in the overall mechanism as explained below, and as illustrated in our suggested mechanistic scheme in Figure 5. At pH=1, the dominant reaction is hydrogen evolution:



At pH=3, the main origin of hydrogen evolution is direct water reduction:



with reaction 1 generating a smaller amount of  $\text{H}_2$  at less negative potential due to diffusion limitations (see Figure 2). This observation is very similar to recent experiments on platinum electrodes<sup>29</sup>. The observation that  $\text{CO}_2$  reduction to  $\text{CO}$  becomes much more dominant at higher pH, must mean that  $\text{CO}_2$  activation does not sensitively depend on the presence of protons, and hence must involve an intermediate that can easily react with water at any pH. Such an intermediate is most likely a negatively charged Brønsted base, and the most obvious candidate for this intermediate is a  $\text{CO}_2$  anion<sup>28,30,31</sup> bound to the Co complex “M”:



which subsequently reacts with water to a metal-bound carboxyhydroxyl intermediate:



The formation of the  $\text{CO}_2^-$  anion normally has a very negative redox potential,<sup>3,8</sup> but may be shifted to less negative potential by the stabilization provided by the coordination of  $\text{CO}_2^-$  to the catalyst. The carboxyhydroxyl intermediate then generates  $\text{CO}$ :



with the  $\text{CO}$  subsequently dissociating from the complex. Due to the presence of the negatively charged intermediate in reaction 4, the pH dependence of this pathway is different from that of the mechanism for reactions 1 and 2, in which no such intermediate is assumed. For reactions 1 and 2, we assume:



and,



which involve concerted proton-coupled electron transfer at every step<sup>32,33</sup>. Reaction 4 is different from the reaction suggested by the DFT calculations of Leung et al., because we specify that the proton donor may be water, rather than  $\text{H}^+$ , due to the basic character of the  $\text{CO}_2$  anion intermediate<sup>23,31</sup>. Note that in this mechanism the reaction rate for  $\text{CO}_2$  reduction itself does not depend on pH, only its relative rate with respect to the hydrogen evolution. Another way of formulating our mechanism is by stating that in the potential window of interest,  $\text{CO}_2$  reduction is approximately zero-th order in proton concentration, whilst hydrogen evolution is first-order in proton concentration.

The further reduction of CO must be slower than its generation, explaining the relatively low overall Faradaic efficiency of  $\text{CO}_2$  reduction to methane. To explain the pH dependence of CO reduction and methane selectivity from  $\text{CO}_2$ , we must assume that CO is reduced to methane without the involvement of negatively charged intermediates. Our experiments also show that an intermediate or byproduct of CO reduction to methane is formaldehyde. Our suggested overall mechanism is summarized in Figure 5.

The above mechanism, which we believe explains our observations consistently, has important implications for future catalyst design. The onset potential for  $\text{CO}_2$  reduction is determined by reaction 3, i.e. by the stabilization of the  $\text{CO}_2$  anion coordinated to the complex. As noted above, the onset potential appears to be related to the  $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$  redox transition, based on cyclic voltammetry<sup>23</sup> and on the previous observation that the  $\text{Co}^{\text{I}}$  oxidation state is the active state for proton reduction<sup>26</sup>. Nielsen and Leung have also concluded, based on literature data and their own DFT calculations, that  $\text{CO}_2$  binds to the  $\text{Co}^+$  state of the porphyrin<sup>23,31</sup>. Therefore, we assume that  $\text{Co}^{\text{I}}$  oxidation state of the CoPP is the catalytically active state. The closer the  $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$  redox potential lies to the overall equilibrium potential, the lower the overpotential for  $\text{CO}_2$  reduction. Reaction 3 is therefore



et al.<sup>9</sup>. Therefore, future calculations must take into account the existence of such intermediates, and should aim at enhancing the stability of the intermediate in reaction 3. Moreover, in order to have a higher overall efficiency towards methane, the rate of the reduction of CO to methane must be enhanced. Presumably the rate of this reaction can be tuned by the binding of CO to the complex. This will also require further experiments and calculations aimed at screening various catalyst alternatives. We also believe that our mechanism provides a possible rationale for tuning the H<sub>2</sub>/CO ratio from electrochemical CO<sub>2</sub> reduction, as was recently reported for Ru-based molecular catalyst in aqueous solution<sup>36</sup>.

A final word on the overpotential and the Turnover Frequencies (TOF) of our catalyst compares to previous work on molecular catalysts for CO<sub>2</sub> electroreduction to CO. From our experiment, we calculate TOFs through the formula [FE for CO production] x [current density/2\*F] / [number of Co-PP per cm<sup>2</sup>]. In Figure 3, the average current densities measured over one hour at potentials of -0.6 and -0.8 V vs. RHE, corresponding to overpotentials of ca. 0.5 and 0.7 V, were 0.08 and 0.16 mA cm<sup>-2</sup> (at atmospheric pressure), respectively. This corresponds to TOFs of ca. 0.2 s<sup>-1</sup> and 0.8 s<sup>-1</sup>. Costentin et al. have recently reported on the enhanced activity of a modified Fe tetraphenylporphyrin for CO<sub>2</sub> reduction to CO in a mixed DMF/water solvent<sup>10</sup>. In their experiment, the porphyrin was in solution. Their measured current densities and corresponding effective CO<sub>2</sub> turnover rates, are very similar to ours, namely 0.3 mA cm<sup>-2</sup> (see Figure 5 in their paper) at a similar overpotential of ca. 0.5 V. Note that this comparison does not take into account that the solubility of CO<sub>2</sub> is considerably higher in DMF-water mixtures than in water<sup>36</sup> leading to correspondingly higher turnover rates in the DMF-water mixture. From a mathematical model for their reactive system including mass transport of the catalyst to the electrode surface, they report a catalytic TOF of ca. 3000 s<sup>-1</sup>. This is a TOF of a homogeneous catalyst corrected for the slow mass transport in their system, and can therefore not be compared directly with the “effective” TOF of our heterogeneous catalyst. However, from the similar real current densities at a similar overpotential, we believe that we can safely state that our immobilized catalyst system has a similar efficiency.

## 2.5. Conclusion

Summarizing, we have shown that a cobalt-protoporphyrin immobilized on a pyrolytic graphite electrode can reduce  $\text{CO}_2$  to CO and even to the 6- and 8-electron products methanol and methane, in a purely aqueous electrolyte phase, with a very moderate overpotential of ca. 0.5 V. The efficiency of our catalyst (i.e. effective rate at given overpotential) compares favorably to best porphyrin-based catalyst reported in the literature<sup>10</sup>. For optimal Faradaic efficiency, i.e. low concomitant  $\text{H}_2$  production, the proton concentration needs to be suitably tuned to the  $\text{CO}_2$  concentration. The pH dependent activity and selectivity are explained by a mechanism in which the initial step of  $\text{CO}_2$  reduction leads to a catalyst-bound  $\text{CO}_2^-$  anion. This intermediate has a strong Brønsted-base character and can abstract a proton from water, thereby leading to an overall reactivity of the  $\text{CO}_2$  reduction whose pH dependence is substantially different from the competing  $\text{H}_2$  evolution. Lowering the potential for the formation of this catalyst-bound  $\text{CO}_2^-$  anion is therefore the key to making a better catalyst with a lower overpotential, and a suitable adjustment of pH will contribute significantly to a high Faradaic efficiency of such a catalyst. The further reduction of CO to methane and methanol is slow due to the weak adsorption of CO to the catalyst, and due to the fact that CO reduction prefers a more acidic environment. These new insights into the mechanism of  $\text{CO}_2$  reduction on immobilized molecular catalysts in aqueous solution provide important design rules for future catalyst improvement.

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