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Research paper

Selective ligand modification of cobalt porphyrins for carbon dioxide electrolysis: Generation of a renewable H_2/CO feedstock for downstream catalytic hydrogenation

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ABSTRACT

Catalytic hydrogenation is an attractive approach to produce green fuels and chemicals. The building blocks for these processes may be effectively produced from renewable power via direct electrochemical reduction of carbon dioxide in an aqueous media. For the first time, the impact of increasing the local proton concentration of cobalt porphyrin was examined by synthesizing new cobalt porphyrins **2**, Co(o-OCH₃)TPP and cobalt porphyrin **3**, Co(o-OH)TPP. Cobalt porphyrins coated on carbon paper converted carbon dioxide and water into a mixture of hydrogen and carbon monoxide in an aqueous electrolyte at near neutral pH. Increasing the local proton availability of the commercial cobalt porphyrin **1**, accelerates hydrogen generation under heterogeneous conditions across the range of potentials tested (-0.85 to -1.5 V vs. Ag/AgCl) and demonstrates high Faradaic efficiencies (ca. 90%) at low over-potentials (ca. 540 mV). The culmination of this work can help identify key parameters that facilitate generation of sustainable reagents for catalytic hydrogenation under practical and scalable conditions.

1. Introduction

Selective and efficient conversion of carbon dioxide (CO_2) to high energy density fuels is paramount for a closed-carbon energy future. Electrochemical CO_2 reduction is an attractive platform for CO_2 reduction as it can be directly integrated with renewable energy sources. The injection of an electron into CO_2 , however, requires highly negative potentials (large energy investment) and the kinetics are quite sluggish under standard conditions [1–3]. On-going investigations have thus been largely focused on the development of synthetic catalysts, regarding the formation of reduction products requiring four or more electrons (i.e. methane, ethanol, oxalate) [4–6]. After several years, this work has resulted in limited success as it has been faced with tremendous inherent challenges involving high over-potentials and complex parallel reactions schemes that hinder overall product efficiencies [7]. In light of these findings, some have shifted focused away from direct electrochemical CO_2 reduction and back to catalytic hydrogenation processes that use H₂ and CO as the feedstock to build larger molecules [8,9]. These catalytic processes can be used to react H₂ and CO with CO2 to generate methane, methanol, formaldehyde, or higher alcohols [10]. In general, hydrogenation processes are far more mature than their electrochemical counterparts and can support excellent energetic efficiencies for carbon intensive molecules [11]. For example, Wang et al. recently reported a very high selectivity for ethanol (30.1%) via CO catalytic hydrogenation using carbon nanotube supported cobalt-copper with a H₂/CO feedstock of 2:1 [12]. Traditionally, the sources of H₂/CO have come from the deconstruction of agricultural feedstock that have large water, land, and nutrient requirements as well as a fundamentally low energy to product conversion efficiency [10]. Alternatively, catalytic hydrogenation could be directly integrated with renewable energy sources by identifying a versatile catalyst that could electrochemically produce a range of H₂/ CO blends (from a waste CO2 feedstock and water) that accommodate a variety of downstream hydrogenation processes. In the early work on

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electrochemical CO₂ reduction, several catalysts with this capability were identified. However, these catalysts were generally not further optimized, in terms of energy efficiency or stability, as H₂ or CO (alone) are relatively low value products. As such, most of these catalysts were discarded and research efforts progressed towards the formation of hydrocarbons. In lieu of this methodology, Hu et al. recently reported that cobalt tetraphenyl porphyrins could produce mixtures of H₂/CO with extremely high efficiencies under heterogeneous conditions [13]. Early work with analogous metalloporphyrins showed that the presence of Lewis acids such as Mg^{2+} or Ca^{2+} could enhance the catalytic CO_2 reduction efficiency and stability of molecules [14,15]. These studies proposed a push-pull mechanism where the electro-reduced metal species pushes an electron pair to the CO₂ molecule and the electrondeficient acid synergist promotes the separation of one of the C-O bonds [16,17]. Following these observations some have demonstrated the organic framework of porphyrins modified by electron withdrawing groups can benefit the electronic structure towards improved CO₂ reduction capabilities [18]. In line with these findings, Costentin et al. found that the electroreduction of CO₂ to CO of an iron-based porphyrin monomer could be greatly enhanced by the addition of hydroxyl groups in all phenyl group ortho positions under homogenous conditions [19]. This and subsequent reports concluded that the local addition of acids assisted in the stability of a key intermediate, $[Metal-(P)-(CO_2)^-, in$ the formation of H₂/CO and therefore improved overall Faradaic efficiencies of the process [19,20]. In the present study, we applied this theory and synthesized new cobalt based catalysts, cobalt porphyrin 2, Co(o-OCH₃)TPP and cobalt porphyrin 3, Co(o-OH)TPP to study the impact of increasing the local proton source on H₂/CO efficiencies under heterogeneous conditions. It is important to note that past studies primarily characterized catalysts under only homogenous conditions, that are not practical for scale-up. The results presented, hereto, demonstrate high yields and efficiencies for a variety of H₂/CO blends using the novel porphyrin catalysts in aqueous conditions. Moreover, this work provides valuable experimental insight on the role of local proton concentration in CO2 electro-reduction and demonstrates a variety of operating conditions to produce tunable H2/CO mixtures that can be coupled to downstream hydrogenation processes towards the generation of green fuels and chemicals.

2. Experimental

Cobalt(II)-5,10,15,20-tetrakis(2',6'-dimethoxyphenyl)-

21H,23H-porphyrin,Co(o-OCH₃)TPP: Solid H_2 (o-OCH₃)TPP (0.1453 g, 0.170 mmol) and anhydrous CoCl₂ (II) (0.441 g, 3.40 mmol) were dissolved in anhydrous tetrahydrofuran (THF, 30 mL) under inert N₂ gas and 2,6-lutidine (0.060 mL, 0.51 mmol) was added. The solution was then refluxed for two hours. After removing THF solution, the mixture was dissolved in dichloromethane (DCM) and washed with deionized water three times [19,21].

Cobalt(II)-5,10,15,20-tetrakis(2',6'-dihydroxyphenyl)-21H,23H-porphyrin, Co(o-OH)TPP: Co(o-OH)TPP was prepared in the same fashion except ethyl acetate was used to dissolve the mixture after removing the THF solution.

2.1. Material characterization

¹H NMR spectra were recorded on a Bruker Avance-III 300 NMR spectrometer. Fourier transform infrared (FT-IR) spectra were measured with an Agilent Technologies, Cary 630. UV–Vis spectra were recorded on an Agilent 8453. ESI-MS measurements were performed on a Synapt G2 HDMS. Elemental analysis of as-obtained compounds was conducted on a CHN analyzer from Exeter analytical (model CE440 CHN).

2.2. Cyclic voltammetry

A platinum wire (BASi-MF-1033) was employed as counter electrode along with an Ag/AgCl reference electrode and the appropriate working electrode (GC disk or carbon paper). 2 mM of catalyst and 0.1 M tetrabutylammonium hexafluorophosphate (NBu₄PF₆) as the supporting electrolyte were added. Prior to analysis, the electrolyte solutions were saturated with high purity Argon or CO₂ gas.

2.3. Gas analysis

Gas samples were obtained directly from the headspace of the electrochemical cell using a 250 μ l gastight syringe (Hamilton-1700 series) and were immediately analyzed on an Agilent Technologies 7890A gas chromatography system equipped with a thermal conductivity detector (TCD) and packed column [22,23].

2.4. Faradaic efficiency calculation

The Faradaic efficiency (FE) of the CO_2 electrochemical reduction products was calculated as

$$FE = \frac{Z \times n \times F}{Q}$$

where n is the number of the electrons needed for CO_2 reduction or HER (2 for both CO and H₂), Z is the moles of products, F is the Faraday constant, and Q is charged transferred during electrolysis.

3. Results and discussion

To examine the impact of local proton availability on CO_2 reduction, we have synthesized two modified cobalt porphyrins 2 and 3 by the addition of phenolic methoxyl or hydroxyl groups in all phenyl group ortho positions (Fig. 1). Their catalytic activity was then compared to the performance of the commercial porphyrin 1. Substitution of hydrogen with methoxy and hydroxyl groups increased the local proton availability. Prior to cobalt-metalation, the structure of the two free base porphyrins, H₂(o-OCH₃)TPP and H₂(o-OH)TPP, were confirmed by nuclear magnetic resonance spectroscopy (NMR) in d-CHCl₃ and d-CH₃OH, respectively (Figs. S1, S2). The as-prepared cobalt porphyrins 2 and 3 were then finished via a final metalation step and characterized by ultraviolet–visible (UV–Vis), Fourier transform-infrared spectroscopy (FT-IR), electrospray ionization mass spectrometer (ESI-MS), thermogravimetric analysis (TGA), and CHN elemental analysis (Figs. S3–S5, Table S1, S2). The analyses confirmed that the



 $R = H(1), OCH_3(2), OH(3)$

Fig. 1. The chemical structure of cobalt porphyrins with modified ligands (2 and 3) and commercial one (1).



Fig. 2. CO_2 reduction capabilities of (a) commercial porphyrin 1; (b) as-obtained cobalt porphyrin 2; (c) as-obtained cobalt porphyrin 3; (d) catalysts comparison. Vertical dashed lines depict shift of onset potentials from aprotic CO_2 conditions (light green) to acid conditions (dark blue). Conditions: Ag/AgCl reference electrode, glass carbon working electrode, Pt anode for counter electrode, 1 mM catalyst, and 0.1 M NBu₄PF₆ dissolved in DMF.

metalation step was effective and the modified cobalt porphyrin **2** and **3** were successfully synthesized. FT-IR spectra of cobalt **2** showed the disappearance of the N–H peak (3300 cm) of $H_2(o-OCH_3)TPP$ and UV–Vis spectra of $H_2(o-OH)TPP$ showed a red shift after metalation. ESI-MS of both as-obtained compounds revealed that the percent error of experimental values was less than 2 ppm from the theoretical, further confirming the structure of these compounds. CHN elemental analysis provided the purity of the as-obtained cobalt porphyrin **2** and **3** and TGA confirmed the presence of several equivalents of solvents molecules, for example, tetrahydrofuran or water.

Cyclic voltammetry (CV) of cobalt porphyrins 1–3 were obtained in a DMF solution containing 0.1 M NBu₄PF₆ saturated with CO₂ gas to assess the fundamental impact of the local proton source on electrocatalytic CO₂ reduction (Fig. 2). Notably, an assortment of responses in catalytic behavior were observed between the catalysts upon introducing varying quantities of protons (2 M, 10 M H₂O) to the initially aprotic solvent. Commercial cobalt porphyrin 1 seemed to be unaffected by the addition of water with a $Co^{2+}-Co^{+1}$ activation peak around -0.80 V vs. Ag/AgCl and the start of a major reduction event s around -1.85 V vs. Ag/AgCl across each scenario. These findings are similar to those of Hu et al. when introducing protons via phenol to CoTPP immobilized on GC disk electrodes in DMF [13]. In contrast, the as-obtained cobalt porphyrins 2 and 3 seemed to show enhanced catalytic activity upon the addition of water. For example, the onset potentials (i.e. potential at which sharp increase in reduction current was observed) of both cobalt porphyrin 2 and 3 seemed to shift by ca. 300 mV to more positive potentials upon adding 10 M H₂O. Remarkably, the reduction current of cobalt porphyrin 3 was much higher than others upon the addition of 10 M H₂O reaching about twice that of cobalt porphyrin 1 and 2 at -2.5 V vs. Ag/AgCl. These findings were supported by similar trends of the Tafel plot constants as the as-obtained catalysts achieved much smaller values in the presence of H₂O owing to their enhanced catalytic activities (Table S4). The culmination of these results are in-line with the findings of others using modified FeTPP catalysts for CO₂ reduction under homogenous conditions [19]. It is important to note that at the potentials near where the activation peaks start, the current can be attributed to CO₂ reduction, hydrogen

evolution reaction (HER) or a mixture of both. Consequently, controlled potential electrolysis experiments were required to investigate the product selectivity of each catalyst and elucidate the affinity for each possible reaction mechanism.

To maintain the practicality of these findings, electrolysis was conducted under heterogeneous conditions with an aqueous electrolyte (at room temperature). Preliminary CVs of each of the catalysts (in aqueous conditions) demonstrated that the onset potentials started at slightly more positive potentials than -0.8 V vs. Ag/AgCl so electrolysis were carried out at moderate potentials in the range of -0.85 V to -1.5 V vs. Ag/AgCl, in order to produce appreciable gaseous products (Fig. S6). At each operating voltage, it was apparent that the as-obtained cobalt porphyrins 2 and 3 favored the HER more than cobalt porphyrin 1 under the same conditions. For instance, the Faradaic efficiencies (FEs) of cobalt porphyrin 1 for HER was only about a tenth of that of cobalt porphyrin 2 and 3 after an hour electrolysis at -1.2 V vs. Ag/AgCl (Fig. 3). This finding is significant as in comparable studies with iron porphyrins (under homogenous conditions) enhanced catalytic waves were attributed to only CO₂ reduction [19]. Under heterogeneous conditions, the selectivity towards CO₂ reduction via the electron push-pull mechanism may have been lessened due to direct competition of the attached acid synergist with the other acids in solution (i.e. CO2 species and H2O). Using highly regarded DFT models [24], it was anticipated that the increased local proton availability would accelerate the stabilization of the cobalt- CO_2 adduct via Eq. (4) as part of the proton-concerted reaction pathway of CO₂ towards CO.

$$[\text{CoP}]^0 + e^- \rightarrow [\text{CoP}]^- \tag{1}$$

$$[\text{CoP}]^- + \text{CO}_2 \rightarrow [\text{Co(P)} - (\text{CO}_2)]^-$$
(2)

 $[\text{CoP}]^0 + \text{CO}_2 + \text{H}^+ + \text{e}^- \rightarrow [\text{CoP} - \text{COOH}]^0$ (3)

$$[\operatorname{Co}(P) - (\operatorname{CO}_2)]^- + \operatorname{H}^+ \to [\operatorname{Co}(P) - (\operatorname{COOH})]^0$$
(4)

As the equilibrium potential for Eq. (4) is small (-0.37 mV vs. Ag/ AgCl), it is likely that this reaction is spontaneous and non-limiting in the potential range tested, thus the impact of increased proton availability was not observed [24]. The local proton source could have been



Fig. 3. Cobalt porphyrin heterogeneous preparative scale electrolysis. Faradaic efficiencies of each catalyst at (a) -0.85 V vs. Ag/AgCl; (b) -1.2 V vs. Ag/AgCl; (c) -1.5 V vs. Ag/AgCl. Hydrogen evolution reaction (HER) in dark blue and CO₂ reduction reaction (CO₂-RR) in light blue. (conditions: Ag/AgCl reference electrode, catalyst deposited on carbon paper working electrode, graphite anode working electrode, 0.5 M KHCO₃ electrolyte). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

used for Eq. (3) but it seems that it was outcompeted by the initial HER Eq. (5) or Eq. (6) (below) [19,24].

$$[CoP]^{0} + H^{+} + e^{-} \rightarrow [Co(P) - (H)]^{0}$$
 (5)

$$[CoP]^{-} + H^{+} + e^{-} \rightarrow [Co(P) - (H)]^{-}$$
 (6)

Minor products such as formic acid may have also been produced but were likely limited by the high over-potential needed to drive the initial reduction reactions (Eq. A.7, A.8) [24].

Interestingly, heterogeneous testing conditions allowed for CO₂ reduction to occur at very low over-potentials for cobalt porphyrin 3 (ca. 540 mV vs. Ag/AgCl). Furthermore, at potentials close to the onset (ca. -0.8 V vs. Ag/AgCl), H₂ pathways were limited and allowed for excellent CO2 reduction efficiencies. For instance, the CO2-RR FE of cobalt porphyrin 3 was improved by ca. 20% when the operating potential was increased from -1.5 V to -0.85 V vs. Ag/AgCl (Fig. 3). Similar results for the commercial porphyrin 1 were also observed and have been previously reported by others under heterogeneous conditions [13,25,26]. Notably, the CO₂ reduction capabilities of the commercial cobalt porphyrin 1 were not improved by addition of local proton sources. This suggests that improving proton-concerted pathways may not be effective in enhancing CO₂ reduction on cobalt porphyrins under aqueous conditions. Nevertheless, overall efficiencies for each of the catalysts for H₂/CO products were excellent (typically ca. 90%) and unique gas blends for each of the catalysts were observed. This holds great promise for the use of these compounds to generate tunable H₂/ CO feedstock for hydrogenation processes (Fig. S8).

4. Conclusion

Cobalt porphyrins modified with hydroxy groups can produce CO and H_2 in an aqueous electrolyte at near neutral pH and at a low overpotential of ca. 540 mV in heterogeneous conditions. Using newly synthesized cobalt porphyrin **2** and **3** catalysts, the impact of increased local proton availability was examined. This led to accelerated H_2 production and suggested that CO production pathways are not proton sensitive in near neutral pH conditions. The culmination of these findings can help pinpoint crucial operational parameters that produce tunable H_2 /CO mixtures, which can be used as sustainable building blocks for green chemical synthesis in a coupled electrochemical-catalytic hydrogenation reaction. Further optimization of the catalysts as well as integration of hydrogenation processes towards hydrocarbon production is currently underway.

CRediT authorship contribution statement

Joshua Jack: Investigation, Formal analysis, Writing - original draft, Writing - review & editing. Eunsol Park: Investigation, Formal analysis, Writing - original draft, Writing - review & editing. Pin-Ching Maness: Investigation. Shaofeng Huang: Investigation. Wei Zhang: Conceptualization, Formal analysis, Supervision, Writing - original draft, Writing - review & editing. Zhiyong Jason Ren: Conceptualization, Formal analysis, Supervision, Writing - original draft, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2020.119594.

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