Khakpour, Reza; Lindberg, Daniel; Laasonen, Kari; Busch, Michael

**CO2 or Carbonates – What is the Active Species in Electrochemical CO2 Reduction over Fe-Porphyrin?**

*Published in:*  
ChemCatChem

*DOI:*  
10.1002/cctc.202201671

Published: 22/03/2023

*Document Version*  
Publisher's PDF, also known as Version of record

*Published under the following license:*  
CC BY-NC

*Please cite the original version:*  
https://doi.org/10.1002/cctc.202201671
Excellence in Chemistry Research

Announcing our new flagship journal

- Gold Open Access
- Publishing charges waived
- Preprints welcome
- Edited by active scientists

Meet the Editors of ChemistryEurope

Luisa De Cola
Università degli Studi di Milano Statale, Italy

Ive Hermans
University of Wisconsin-Madison, USA

Ken Tanaka
Tokyo Institute of Technology, Japan
Introduction

Electrochemical reduction of CO$_2$ allows to convert carbon dioxide into value-added chemicals or feedstocks.\cite{1,2} In aqueous solution, the CO$_2$ reduction reaction (CO$_2$RR) is always in competition with the hydrogen evolution reaction (HER).\cite{3} The situation is further complicated by the rather low reactivity of CO$_2$. Thus, developing electrocatalysts with high selectivity, stability, and activity possess a substantial challenge.\cite{4–9}

In general, solid state electrocatalysts such as metallic Cu or Ag are considered as the most promising materials for the CO$_2$RR.\cite{10–14} But in recent years also single metal catalysts sites have been proposed.\cite{15–17} For example, single-site catalysts based on Zn, Ni, Fe or Co were found to combine a good selectivity for CO formation and a reasonably high activity.\cite{18–21} A promising alternative to heterogeneous catalysts are molecular electrocatalysts.\cite{22–26} A major advantage of metal-organic compounds is the possibility to fine tune the electronic structure for optimal activity and selectivity through selecting suitable ligands.\cite{27,28} In addition to this, their well defined structure also enables the direct comparison between experimental and computational modelling which is crucial for mechanistic studies.\cite{29–32} Indeed, this is rarely case when dealing with solid catalysts where in-situ formed defects or impurities can be critical to the observed activity.\cite{33,34} Typical examples of homogeneous CO$_2$RR catalysts are Mn, Fe or Co metal cores surrounded by bipyridin, terpyridin, CO or porphyrin\cite{35} type ligands.\cite{29,36} It has been reported that ligands with the ability to form an intramolecular hydrogen bond between a hydrogen donor site and adsorbed CO$_2$ display an increased current density.\cite{37}

While significant efforts have been made to develop design criteria for the catalyst itself in recent years,\cite{38,39} significantly less is known regarding the second potentially critical aspect of electrochemical CO$_2$ reduction, the active species. A typical pH neutral electrolyte for CO$_2$ reduction consists of a mixture of CO$_2$, carbonic acid (H$_2$CO$_3$) and bicarbonate (HCO$_3^-$) and CO$_2$ to be equally likely. However, owing to a very high activation barrier for the initial adsorption of CO$_2$ onto the catalyst, bicarbonate and carbonic acid reduction are found to be several orders of magnitude faster. These data are used to model the pH dependence of the reaction rates of the different reactants. These results confirm that carbonic acid and bicarbonate are the most likely reactants independent of the pH and reactor setup.
Furthermore, Dunwell et al. proposed, using isotopic labeling, that HCO$_3^-$ increases the rate of CO$_2$RR to CO and that bicarbonate is the carbon source for CO$_2$RR. They explained these measurements by a fast equilibrium between CO$_2$ and HCO$_3^-$ in the double layer close to the catalyst which results in the formation of CO$_2$ which is then reduced. Very similar results were also observed by Zhu et al. over Cu.

However, no direct proof for such a mechanism is provided by the authors. Thus, their results could also be interpreted as a first indication of the direct reduction of bicarbonate. Additionally, some experiments suggested that the product distribution strongly depends on the pH which in turn could indicate that different carbonate species and CO$_2$ display different reactivity.

However, despite these indications a final proof that carbonate species indeed contribute to the overall CO$_2$RR is still missing. This lack in our understanding is problematic since different reactants can proceed through different reaction intermediates which in turn can affect design criteria for the most optimal catalysts. It is therefore the aim of this work to shed light on this question by exploring the reactivity of CO$_2$ and different carbonate species over a Fe porphyrin model catalyst (Fe(pppy); Figure 1a) using density functional theory modelling. Building on these data, we will then model the pH dependence of the total activity to identify the most active species under different reaction conditions.

**Results and Discussion**

Let us start the discussion with the identification of the active species of the Fe(pppy) catalyst under reaction conditions. Depending on the electrochemical potential at the cathode, the Fe(pppy) complex may exist in a formal Fe(II), Fe(I), Fe(0) or even Fe(−I) oxidation state. Note that these oxidation states are only formal and therefore do not necessarily correspond to the true charge at the Fe ion. According to our DFT computations a potential of −1.22 V vs. the standard hydrogen electrode (SHE) is needed to reduce Fe(III)(ppy) to Fe(I)(ppy). This transition overlaps with the experimentally observed onset for CO$_2$ reduction in Fe doped porphyrinic or pyrrolic graphene in water. Fe(I) is then converted to Fe(0) at a potential of −1.48 V vs. SHE while the reduction to Fe(−I) requires an even lower potential of −1.54 V vs. SHE. Water was found to bind only very weakly to the complex in all cases. Thus, assuming a potential between −1.2 V and −1.4 V vs. SHE an uncoordinated Fe(I) is most likely the active species for electrochemical CO$_2$RR in water. This assessment agrees also well with evidence from X-ray absorption spectroscopy for Fe single atom catalysts.

Assuming a pH of 7 which is commonly used for CO$_2$RR in water, the Fe(I)(ppy) complex may react either with CO$_2$, HCO$_3^-$ or H$_2$CO$_3$, CO$_2$ to the other hand is only present in very minor amounts under these conditions but has nevertheless been included in this study for the sake of completeness. If we assume CO$_2$ as reactant, the reaction may either proceed through the direct adsorption at the metal site (Equation (2)) and Figure 1b; red path (I)) or react with a Fe−H hydride (Equation (3) and Eq. (4)) (See SI for other potential mechanisms of CO$_2$RR).

\[
\text{(2)} \quad \text{N} \xrightarrow{\text{Fe(ppy)}} \text{N} + \text{CO}_2 \xrightarrow{\text{N} \xrightarrow{\text{Fe(ppy)}} \text{N}} \text{N} \xrightarrow{\text{Fe(ppy)}} \text{N} + \text{N} \xrightarrow{\text{Fe(ppy)}} \text{N} + \text{OH}^-
\]

\[
\text{(3)} \quad \text{N} \xrightarrow{\text{Fe(ppy)}} \text{N} + \text{H}_2 \xrightarrow{\text{Fe(ppy)}} \text{N} + \text{H} \xrightarrow{\text{Fe(ppy)}} \text{N} + \text{HCO}_3^-
\]

Owing to the redox potential of −1.53 V vs. SHE and a high activation energy of 1.78 eV, hydride route (Equation 3) and subsequent H$_2$ and formate formation (Equation 4) are, in line with experimental studies, surpassed in the assumed potential range of −1.2 V to −1.4 V vs. SHE. However, a more negative potential results in the formation of Fe("0")(ppy) which displays a much lower activation barrier of 0.88 eV and thus, in principle allows for at least slow H$_2$ formation.

This leaves the direct reaction of CO$_2$ with the metal site as the only possible path to direct CO$_2$ reduction. Considering all possible CO$_2$ adsorption geometries, Fe−COO intermediate was identified as the only stable configuration (Figure 1b; red path (I)). Owing to the high stability of gas phase CO$_2$ this step is both thermodynamically and kinetically demanding. It is therefore unsurprising, that the adsorption of CO$_2$ is slightly endergonic by 0.17 eV (Figure 2a). In addition to these somewhat unfavourable thermodynamics also a high barrier of 0.95 eV needs to be overcome (TS1 in Figure 2a) which renders it overall sluggish. In principle this high activation barrier could be overcome by an increase in temperature. However, this would at the same time also increase the entropic penalty on
the thermodynamics of the carboxylate formation step and thus, render the Fe−COO intermediate even less stable.

The Fe−COO carboxylate is then protonated in a subsequent PCET step to form a Fe−COOH species (Figure 1b; red path (l)). This reaction requires a potential of −0.65 V vs. SHE (Figure 2a). Assuming, on the other hand, a decoupled proton transfer (PT) and electron transfer (ET) changes the picture significantly.\[66]\] If we assume the reaction to be initiated by a proton transfer, the protonation of Fe(I)−COOH to form Fe(I)−COOH$^+$ is endergonic by +0.19 eV at pH 7 which corresponds to a pKₐ of 4. This direct protonation of Fe(I)−COOH is, therefore, unlikely. An electron transfer, on the other hand, activates Fe(I)−COO species for the proton attack. The reduction of the formal Fe(I)−COO to a formal Fe(I)−COOH$^+$ requires a potential of −1.09 V vs. SHE (Figure 2a). The subsequent PT step, from 2b to 3, is then fairly exergonic by −0.44 eV at pH 7 which corresponds to a pKₐ of 10. Thus, Fe(I)−COOH will remain protonated at pH 7 (Figure 2a and 1b; red path (l)). Furthermore, only a minor barrier of 0.30 eV needs to be overcome for the proton transfer from H$_2$O$^+$ (transition state TS2 in Figures 1b and 2a). Naturally, changing the proton source from H$_2$O$^+$ to H$_2$O will increase the activation energy slightly. Next, an additional OH group can be eliminated as water to form Fe−COOH which then desorbs as CO (Figures 1b). Indeed, Fe porphyrins are known to be selective towards CO formation.\[39,\[70]\] The protonation of Fe(I)−COOH followed by water elimination and CO desorption reactions are exergonic by −0.18 eV and −0.83 eV, respectively (Figures 1b). This is then followed by the recovery of the Fe(I)−ppy from Fe(II)−ppy catalyst through an electrochemical reduction reaction which requires a potential of −1.22 V vs. SHE. In summary, the conversion of CO$_2$ to Fe−COOH over Fe(II)−ppy requires an activation energy of 0.95 eV for the adsorption of CO$_2$ (TS1) and has an onset potential of −1.22 V vs. SHE.

A potential alternative to the kinetically unfavourable direct reduction of CO$_2$ is the reduction of H$_2$CO$_3$ or HCO$_3^−$. The reaction paths of all potential reactants (CO$_2$, H$_2$CO$_3$, HCO$_3^−$) meet with the formation of the Fe−COOH intermediate (Figure 1b). All attempts to bind carbonate species directly to the Fe site through the carbon failed owing to the unstable complex e.g. they immediately desorbed owing to the lack of any sizable barrier and unfavourable thermodynamics. In the case of the interaction between Fe and the COO of bicarbonate, we were only able to find a very weak van der Waals interaction as indicated by a rather long Fe−O distance of 3.02 Å. However, the overall reaction possesses significant similarities to a second order nucleophilic substitution reaction (S₂). These reactions are of central importance to organic synthesis\[71,\[72]\] and proceed through a concerted bond formation between a nucleophile under elimination of a suitable leaving group. In addition, the S₂ mechanism has previously been suggested by Koide et al. for an electrochemical cobalt-carbon bond formation in metalloporphycene.\[73\] In the present case, Fe will act as nucleophile through one of its free electron pairs. At the same time, an OH group will become protonated and is eliminated as H$_2$O. This reaction is exemplified for carbonic acid (Eq. 5).

The protonation of OH groups to form a sufficiently active H$_2$O leaving group is common in organic chemistry.\[74,\[75]\] Since this protonation is a pure acid base reaction, it can be expected to display a very low activation barrier.\[76\] Under typical experimental conditions (water, pH 7), H$_2$O$^+$, water bicarbonate or carbonic acid may react as proton donors.

Assuming H$_2$O$^+$ as a proton donor, the S₂ reaction is slightly exergonic by roughly −0.6 eV for both bicarbonate and carbonic acid (Figure 2b and 2c). The reaction becomes less exergonic or even endergonic if a weaker acid like carbonic acid (pKₐ = 3.88)\[70\] or bicarbonate (pKₐ = 10.33)\[77\] is considered. For carbonic acid, the reaction remains exergonic by approximately −0.5 eV while it becomes endergonic by ≈0.5 eV if bicarbonate is assumed as proton donor. For water the reactions become strongly endergonic by ≈0.9 eV. Owing to this dependence of the reaction energetics on the pKₐ of the proton donor at least
a weak acid must be added to activate H$_2$CO$_3$ or HCO$_3^-$ reduction which limits the pH of the electrolyte to acidic or neutral conditions.

Initial attempts to compute the activation barrier for this initial step for H$_2$CO$_3$ and HCO$_3^-$ reduction using the standard transition search algorithms failed. We therefore decided to split the S$_2$ reaction into two steps for which we were able to perform potential energy surface (PES) scans (see SI for all scans). In the first step, we assumed the bond formation between the reactant and the active species. E.g. we scanned along the Fe–C (Figure 1b; TS3) bond. We then protonated the OH leaving group and scanned along the C—OH$_3$ bond (Figure 1b; TS3) assuming a fixed Fe–C bond length of 2.4 Å. The influence of the proton transfer on the transition state was neglected owing to the already considerable instabilities in the transition state search. This can be justified since this step is a pure acid-base reaction which can be expected to be fast.

Owing to these assumptions, the reported activation barriers correspond to an upper boundary and the true activation barrier might even be lower if the breaking of the C–OH$_2$ and the formation of the Fe–C bond occur in a concerted step. Using this procedure, we do not find any sizable barriers for the individual Fe–C bond formation and the C–OH$_3$ bond breaking steps. Instead, the initial step of Fe–C bond formation is slightly endergonic by 0.38 eV ($\text{H}_2\text{CO}_3$) and 0.47 eV (HCO$_3^-$). The subsequent C–OH$_2$ bond breaking on the other hand is exergonic by around −1.02 eV for both H$_2$CO$_3$ and HCO$_3^-$ assuming a H$_2$O$^+$ proton donor (see SI). Thus, a barrier of not more than $\approx$0.38 eV and $\approx$0.47 eV must be overcome for carbonic acid and bicarbonate reduction, respectively. The elimination of OH$^-$ without protonation on the other hand is kinetically almost impossible owing to a highly unfavourable Fe–C–OH bond breaking which requires an energy of 0.12 eV (H$_2$CO$_3$) and 0.76 eV (HCO$_3^-$). This indicates the importance of the OH protonation before C–OH bond breaking. Apart from the solution, modification of the Fe(ppy), for example by phenolic groups, can provide the required proton through an intramolecular proton transfer.

The initial S$_2$ reaction is then followed by an ET step. For H$_2$CO$_3$, this redox reaction requires a potential of $\approx$0.69 V vs. SHE and results in the formation of Fe(II)−COOH where the CO$_2$ reduction and carbonic acid reduction pathways meet (Figures 1b and 2b). For HCO$_3^-$ reduction a lower potential of $\approx$1.09 V vs. SHE is needed to form Fe(II)−COO (Figures 1b and 2c). Once this point in the mechanism has been reached, all subsequent steps for HCO$_3^-$, H$_2$CO$_3$ and CO$_2$ reduction become equivalent. Accordingly, the formation of Fe(II)(ppy) is followed by a hydrogrogenation to form Fe(II)(pppy) which requires a potential of $\approx$0.44 V vs. SHE and an activation barrier of 0.30 eV.

Having said this, also the HCO$_3^-$ and H$_2$CO$_3$ reduction requires the same onset potential of $\approx$1.22 V vs. SHE as the competing CO$_2$ reduction which renders them indistinguishable. This is due to the fact that the discussed reaction pathways (Figure 1b; paths (I, II, III)) all result in the recovery of Fe(II)(ppy) and Fe(III)(ppy) catalyst. However, taking also the kinetics of the respective reaction paths into account, HCO$_3^-$ and H$_2$CO$_3$ reduction are significantly more favourable than CO$_2$ reduction. This can be rationalized when considering that both bicarbonate and carbonic acid already possess O=C–O bond angles which are close to what is required for the formation of the Fe–COO or Fe–COOH intermediates. Thus, these species could also be viewed as an activated form of CO$_2$. Overall, HCO$_3^-$ and H$_2$CO$_3$ reduction instead of CO$_2$RR increase the rate of CO formation. This is in line with the experimental study by Dunwell et al. where bicarbonate was found to contribute to an increased CO$_2$RR rate. Our results are also in agreement with the work of Zhu et al. who observed a Cu−COO intermediate through attenuated total reflectance surface enhanced infrared absorption spectroscopy (ATR-SEIRAS). The source for this intermediate was found to be bicarbonate based on isotope labeling. Similar observations were also made by Dunwell et al. Both groups speculated that this species originated from the fast CO$_2$/HCO$_3^-$ equilibrium in the double layer close to the surface. However, no proof for such a mechanism is provided by them. In our mechanism on the other hand the Fe−COO intermediate is directly formed from bicarbonate through the S$_2$ mechanism at the catalyst (Figure 1b; path III).

Proofing this direct mechanism would require to quench any interconversion between CO$_2$ and the carbonate species. This could for example be achieved in a non-aqueous solvent.

So far, only activation barriers were considered. However, under realistic conditions also the concentrations of the reactants will enter the total reaction equation. In the present case, the reduction of CO$_2$ will be first order with respect to the concentration of CO$_2$ and the catalyst Fe(II)(ppy). For bicarbonate and carbonic acid, on the other hand, also the proton donor (e.g. H$_2$O$^+$ or H$_2$CO$_3^-$) concentration will enter the equation since it is needed for the elimination of water. A more detailed description of the models can be found in the SI.

In Figure 3, a summary of the speciation of CO$_2$ and the carbonic acid species is shown assuming two distinct situations. The first situation correspond to that of a simple bicarbonate electrolyser in which a 0.1 M carbonate solution is created under atmospheric conditions (pressure (p) 1 bar air; maximum concentration of CO$_2$ in solution, [CO$_2$]$_{\text{sol}}$ = 350 ppm; Figure 3a). The resulting concentration profile is qualitatively identical to the Bjerrum plot known from marine chemistry. Assuming an open system in which CO$_2$ can enter the gas phase once the solubility limit is reached, CO$_2$ is the majority species under strongly acidic conditions.. But even under these conditions, it is only present in rather low concentrations of approximately $10^{-6}$ M. Already at a pH of 4, the bicarbonate concentration becomes significantly larger than that of CO$_2$. Nevertheless, the CO$_2$ concentration remains approximately constant up to a pH of 6 due to its rather low solubility after which it quickly drops. Carbonic acid is linked to CO$_2$ through a pH independent hydration reaction and thus, possesses an equivalent concentration profile as CO$_2$. Owing to unfavourable energetics, its concentration is roughly 2 orders of magnitude lower. Bicarbonate is finally the majority species up to a pH of $\approx$10 after which carbonate takes over.

The speciation can be used to explore the pH dependence of the reaction rate for the different reactants (Figure 3a). In line with the high activation barrier, we find that the reduction of...
CO₂ is, even at very low pH, where CO₂ is still the majority species, extremely slow. Indeed, H₂CO₃ is by far the most reactive species under these conditions. Moving towards higher pH, the rate for CO₂ and HCO₃⁻ reduction remains approximately constant up to a pH of ≈ 6 after which they start to drop. The reason for this drop is the reduced concentration of CO₂ or proton donors in the electrolyte. Carbonic acid on the other hand only displays a very high activity at very low pH which then quickly drops until it becomes even less reactive than CO₂. The origin of this quick decrease is the decrease in both the H₃O⁺ and H₂CO₃ concentrations at higher pH.

The second model describes a situation which may be observed at a gas diffusion electrode. Here, we assumed a CO₂ pressure of ≈ 1 bar. Assuming this model we observe a rather high concentration of 0.032 M CO₂ in the electrolyte which is independent of the pH (Figure 3b). Naturally, this renders also the carbonic acid concentration pH independent since the interconversion between both species does not involve any protons. Bicarbonate and carbonate on the other hand only displays a high activity at very low pH which then quickly drops until it becomes even less reactive than CO₂. The origin of this quick decrease is the decrease in both the H₃O⁺ and H₂CO₃ concentrations at higher pH.

Despite this very different concentration profile and the much higher concentration of CO₂, we still do not observe any significant contribution of it to the overall activity. Instead, the reactivity is again completely dominated by bicarbonate and carbonic acid (Figure 3b). Identical to the previous case we again find carbonic acid to dominate under more acidic conditions whereas bicarbonate is more active at neutral pH. It is noteworthy that, in contrast to the electrolysis of the carbonate electrolyte, now no significant drop in activity is observed for the reduction of H₂CO₃. The reason for this is the pH independent concentration of H₂CO₃ in the electrolyte which can act both as reactant and proton donor and thus, replace H₃O⁺ at higher pH. Furthermore, the activity of bicarbonate constantly rises with an increase in the pH. The reason for this is the monotonous but potentially unphysical increase of the bicarbonate concentration. Additionally, carbonic acid can again take over the role of the proton donor in the initial adsorption through an Sn₂ reaction. Overall we find bicarbonate and carbonic acid reduction to be at least 5 orders of magnitude faster than the competing CO₂ reduction. Thus, even at gas diffusion electrodes bicarbonate and carbonic acid reduction are likely the most active paths towards "CO₂" reduction.

**Conclusion**

In summary we have compared the initial steps of the "CO₂" reduction reaction assuming CO₂, bicarbonate and carbonic acid as potential reactants. Our computations clearly show that the reduction of CO₂ over Fe(ppy) is kinetically hindered while the reduction of H₂CO₃ and HCO₃⁻ are kinetically and thermodynamically favourable. Their reduction is initialized by a Sn₂ type reaction in which a Fe-C bond is formed while at the same time an OH group is eliminated as water after protonation. In a typical electrolyte both H₂O⁺ or weak acids such as H₂CO₃ may act as proton donors. Owing to the significantly higher activation barrier for direct reduction of CO₂, the overall

---

**Figure 3.** a) A simple bicarbonate electrolyser with a 0.1 M carbonate solution atmospheric conditions and b) gas diffusion electrode with constant gas pressure of 1 bar CO₂. (Details of the models can be found in the SI.)
kinetics are independent of the pH and the reactor setup, determined by the reduction of $\text{H}_2\text{CO}_3$ and $\text{HCO}_3^-$.

**Computational Details**

All density functional theory (DFT) computations were performed using Gaussian 16 Rev C.01. In all cases the M06$^{[80,81]}$ functional in combination with a triple zeta Def2-TZVP$^{[82]}$ basis set was used. This DFT functional was found to perform best for transition metal doped porphyrins considered in this study.$^{[83]}$ The integration grid was set to „ultrafine”. The solvation effects in water were modeled using the SMD implicit solvation model.$^{[84]}$ The structures were considered converged to the ground state if no imaginary frequencies were present while transition states were confirmed by the presence of exactly one imaginary frequency. Transition state optimizations were performed using the quasi-stationary transition 3 (QST3) method. In cases where we were unable to identify the transition state through the QST3 method, potential energy scans (PES) were used instead. To reduce the computational cost for this large number of computations, we opted for the cheaper M06L meta-GGA functional. This method is found to display a comparable accuracy for porphyrins as the much more expensive M06 functional.$^{[83]}$

The spin state was tested for all intermediates using a Def2-SVP basis set. The energetically most favourable state was then used to construct the reaction profiles. The computations used here were repeated using the Def2-TZVP basis set. To ensure consistency, the spin states were only allowed to change by 1/2 upon reduction by an additional electron while identical spin states were used for purely chemical steps. Redox potentials of proton coupled electron transfer steps are computed using the computation normal hydroxide electrode approaches which uses $\text{H}_2\text{O}$ in the gas phase as reference. pKa values were computed using the isodesmic method (Eq. (6))$^{[86,87]}$ and scaled by Eq. (7) to correct for the shortcomings of the SMD solvation model.$^{[88]}$

\[
\text{pKa} = \frac{\Delta G_{\text{isodesmic}}}{RT} \ln(10) + \text{pKa(Ref.)}
\]  
\[
\text{pKa(scaled)} = 0.49 \times \text{pKa(DFT)} + 3.2
\]

Following previous work formic acid (pKa = 3.77)$^{[90]}$ was used as reference.

For pure electron transfer steps that were not followed or proceeded by an acid-base reaction the effective absolute potential method$^{[91]}$ with formic acid as reference compound was used which allows for optimal cancellation of errors.$^{[92]}$ Using this method we found an effective absolute potential of electron was calculated as $-4.06 \text{eV}$. Note that these effective absolute potentials can differ significantly from the values reported in literature.$^{[93]}$

**Acknowledgements**

Calculations were performed at the Finnish IT centre for science (CSC). All authors acknowledge financial support from the Jane and Aatos Erkko Foundation through the “Renewable energy storage to high value chemicals” project. M.B. is additionally grateful for the support through the Dr. Barbara Mez-Stark foundation. Open Access funding enabled and organized by Projekt DEAL.

**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** Bicarbonate · CO2 reduction · Electrocatalysis · Hydrogen evolution · Porphyrin
