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Electrocatalytic CO2 reduction toward liquid fuels : on heterogeneous electrocatalysts and heterogenized molecular catalysts

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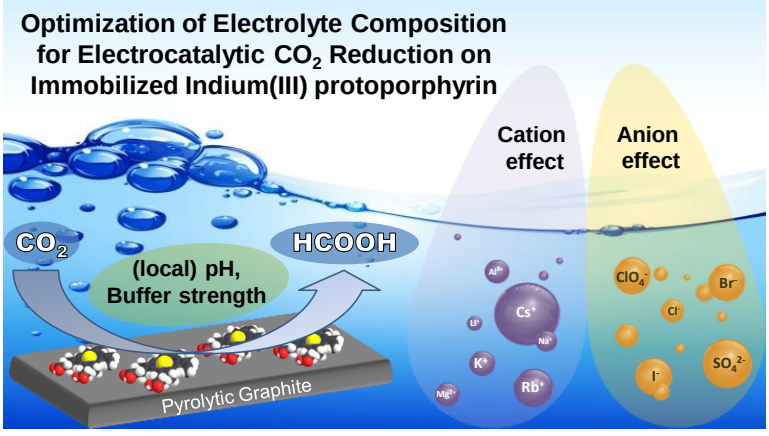
CHAPTER 7

Optimization of Electrolyte Composition for Electrocatalytic CO_2 Reduction on Immobilized Indium(III) protoporphyrin



This chapter is based on the article:
Yuvraj Y. Birdja, Olha Nahorna and Marc T. M. Koper, in preparation

Abstract

In this work, we investigate the performance of CO_2 electroreduction on indium(III) protoporphyrin IX immobilized on pyrolytic graphite in different electrolyte solutions. We demonstrate the importance of the electrolyte composition and buffer capacity for high selectivity and reactivity toward formic acid. A significant enhancement of the faradaic efficiency in unbuffered electrolytes is obtained, reaching values of FE $\approx 96 \pm 3$ % toward formic acid, which is the result of a combined effect of the electrolyte pH and buffering strength. A cation- or anion effect as has been observed for heterogeneous electrocatalysts or homogeneous molecular catalysts in aprotic solvents, is absent, which indicates the relevance of the nature of the solvent, type of catalysis and reaction path for the impact of electrolyte composition on the selectivity and activity of electrochemical CO_2 reduction. Moreover, we found that the destabilization of the immobilized indium(III) protoporphyrin IX may be more pronounced depending on the electrolyte composition and buffering strength.

7.1 Introduction

Electrocatalytic CO_2 reduction (CO_2RR) is an attractive way toward a sustainable carbon cycle, utilizing renewable energy sources. Decarbonization and electrification of the current energy systems, and intermittency of renewable energy sources can be addressed simultaneously.[1,2] In the last couple of decades, research activity has focused primarily on the design, synthesis and optimization of various electrocatalysts aimed at high selectivity, reactivity and stability of CO_2RR. Additionally, reaction- and process parameters such as the nature of the solvent, ionic species in the electrolyte, buffering strength of the electrolyte, and CO_2 partial pressure, have been identified to play an important role on CO_2RR performance, but have received little systematic attention.

In the late '80s, the electrolyte was shown to impact CO_2 reduction on metal electrodes.[3,4] However, the exact cause of this influence is still not clear, since the effects cannot conclusively be ascribed to pH changes, buffering effects, or cationic/anionic species in solution. Recently, systematic studies have been initiated on these specific factors.[5–14] Kas et al. and Varela et al. demonstrated the change in product selectivity of CO_2RR on copper electrodes by changing the buffer strength.[6,7] Although ionic species also have been shown to influence CO_2RR, there is no consensus yet in the literature about the actual cause of these effects.[8–13] Moreover, we recently found that liquid CO_2RR products can be observed from Cannizzaro-type reactions instead of from direct CO_2RR, due to a local alkaline pH in the vicinity of the electrode, manifested in weakly- or unbuffered electrolytes.[15] Studies regarding the aforementioned parameters have mainly been performed on heterogeneous electrocatalysts.

Savéant and coworkers reported improved catalyst stabilization and a promoting effect by specific ionic species on CO_2RR by iron porphyrins under homogeneous conditions in DMF.[16,17] Heterogenized molecular catalysts have gained in popularity due to the small amount of catalyst needed, the absence of solubility issues in aqueous media, and the more attractive prospects for industrial scale up of the CO_2RR process compared to dissolved catalysts.[18,19] The influence of the electrolyte composition, ionic species, buffer strength has not been studied systematically for heterogenized molecular catalysts to date. Recently, we found that metalloprotoporphyrins immobilized on pyrolytic graphite (PG) are able to efficiently reduce CO_2 to CO or HCOOH depending on the metal center, applied potential and electrolyte pH.[20,21] Moreover, we found that the selectivity, activity and stability are strongly affected by the nature of the substrate, its pretreatment and the catalyst chemical environment.[22]

In this work, we study the effects of electrolyte composition on the selectivity and reactivity of CO_2RR on heterogenized molecular catalysts. As a model system we use indium(III) protoporphyrin IX (InPP) immobilized on PG, which previously has been found to produce formic acid with high faradaic efficiency. In this comparative

study, we demonstrate the influence of the electrolyte, ionic species, and buffering effects on the CO_2RR performance.

7.2 Experimental

For the electrochemical experiments, we used a conventional two-compartment cell ("H-cell") in a three-electrode configuration, where a nafion membrane (Nafion 115) separated the working electrode (WE) and counter electrode (CE) compartments. Pyrolytic graphite was used as WE on which indium(III) protoporphyrin IX was immobilized. Details can be found in the SI and in our previous work.[21] A platinum gauze and reversible hydrogen electrode were used as CE and reference electrode respectively. Current densities reported in this work are normalized by the geometric surface area of the WE, and potentials are corrected for ohmic drop. Generally, potentiostatic bulk electrolysis was performed at E = -1.5 V vs. RHE for 90 minutes, with analysis of collected samples at specific times by High Performance Liquid Chromatography. In this work we distinguish between initial and final pH, which refer to the bulk pH measured respectively before and after CO_2 saturation.

7.3 Results and Discussion

We compare the selectivity and activity of CO_2RR on immobilized InPP on PG in four electrolyte solutions with different anions and buffer capacities, *viz.* phosphate buffer, bicarbonate buffer, borate buffer and potassium chloride electrolyte, each with an initial pH $\approx$ 8.7 and similar concentration of 0.1 M. As shown in Figure 7.1a, very significant differences in faradaic efficiency (FE) can be observed. Bicarbonate buffer and borate buffer solutions lead to respectively the most and least selective HCOOH formation. Although the initial pH was kept the same, the bulk pH after CO_2 saturation is slightly different between the electrolyte solutions as shown in Figure D.1a. Interestingly, the trend in the final pH between the three electrolytes ($pH_{borate} < pH_{phosphate} < pH_{bicarbonate}$) is similar to the trend in faradaic efficiency between these electrolytes ($FE_{borate} < FE_{phosphate} < FE_{bicarbonate}$), which would indicate a possible pH effect, where higher FE is favored by more alkaline final pH. However, the KCl electrolyte does not follow this trend, since the final pH is much lower than that of the remaining electrolytes (Figure D.1b), while the HCOOH selectivity in KCl is higher compared to phosphate and borate buffers. The lower final pH for the KCl electrolyte is obvious, since KCl is not a buffer. For comparison of the stability, we looked at the FE normalized by the initial value, as shown in Figure 7.1e. Besides lowest selectivity, borate buffer also has the lowest stability, while the stability is similar in the other electrolytes. Furthermore, we observe in Figure 7.1b-d that the CO_2RR activity also depends on the electrolyte composition. The bicarbonate electrolyte facilitates the highest activity, while borate buffer leads to very low activity for CO_2RR. Moreover, the HER current

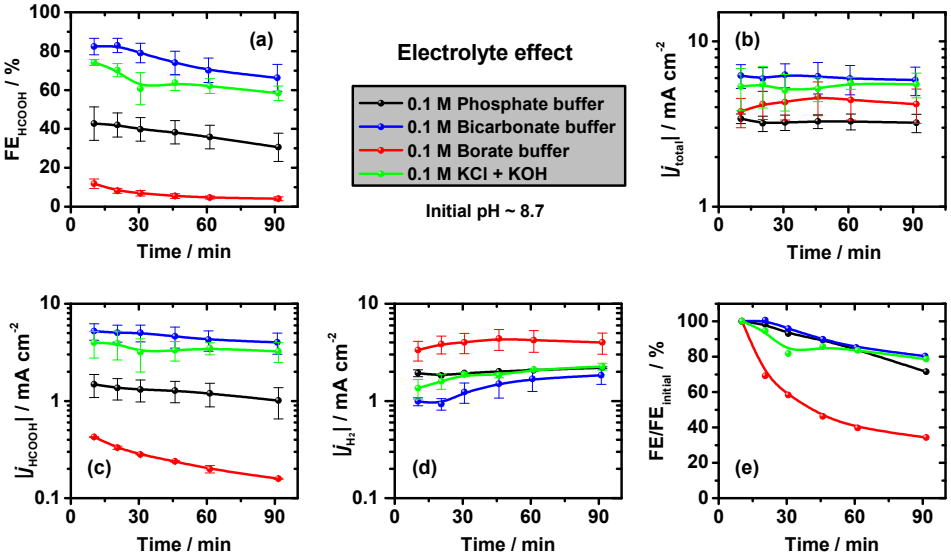


Figure 7.1 (a) Faradaic efficiency toward HCOOH, (b) absolute total current density, (c) absolute partial current density for HCOOH, (d) absolute partial current density for H_2, (e) stability during CO_2 reduction on immobilized InPP in different electrolytes of initial pH $\approx$ 8.7. Lines to guide the eye.

is suppressed in $KHCO_3$, which suggests an additional influence of bicarbonate as reported before.[23,24] Dunwell et al. argued that bicarbonate increases the concentration of CO_2 dissolved in the electrolyte by forming a so-called bicarbonate-CO_2 equilibrium complex.[23] Note that they do not imply that bicarbonate is the active species. Experiments and simulations performed by Hashiba et al., showed an improvement in the limiting CO_2 flux to the electrode surface in bicarbonate buffer compared to KCl and phosphate buffer.[24] Wuttig et al. reported on the sluggish buffering capability of bicarbonate, which acts as a proton donor past the rate-limiting step of CO_2RR on gold.[25] Since borate buffer also performs much worse compared to the unbuffered KCl electrolyte, it is unlikely that the buffering capability of the electrolyte is a necessity for high CO_2RR selectivity.

Due to the interesting performance in KCl electrolytes, and the possible influence of the pH on the performance, we investigated CO_2RR in different KCl electrolytes, where the initial pH was varied by addition of KOH to the solution. As shown in Figure 7.2a, a similar possible correlation is observed as for the three buffer electrolytes, where a more alkaline final pH leads to higher HCOOH selectivity. Figure 7.2b shows that the activity also follows a similar pH dependence as the faradaic efficiency. However, it is clear that a highly alkaline pH is not the key to high selectivity, since a 0.1 M KOH solution leads to lower HCOOH selectivity. Therefore we believe that the pH is an important, but not the only factor influencing

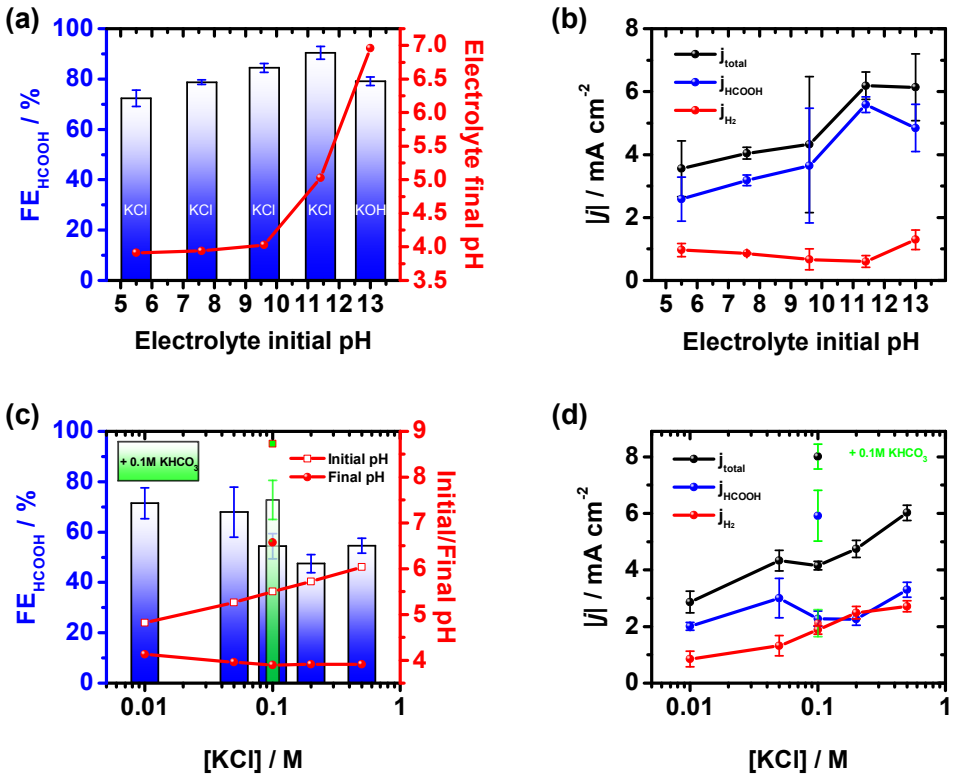


Figure 7.2 Faradaic efficiency toward HCOOH during 10 minute CO_2 reduction on immobilized InPP in (a) 0.1 M KCl electrolyte of different initial pH by addition of KOH and (c) KCl electrolytes of different concentrations. Corresponding total current density and partial current densities for HCOOH and H_2 in (b) and (d).

the selectivity toward HCOOH. Moreover, we studied the influence of different KCl concentrations on the selectivity and activity of CO_2RR as shown in Figure 7.2c-d. These different concentrations of KCl affect the pH of the electrolyte, and it can be seen that the FE again follows the trend of final pH of these electrolytes, which is in agreement with the KCl electrolytes as shown in Figure 7.2a. Interestingly, when 0.1 M $KHCO_3$ is added to 0.1 M KCl (shown in green in Figures 7.2c-d), the selectivity and activity are significantly increased, in agreement with the presumed promoting effect of bicarbonate as discussed before. It is noteworthy that in principle, after CO_2 saturation, a bicarbonate buffer is formed regardless of the electrolyte composition, albeit with different buffering strength or pH.

In our previous work, we observed a difference in the amount of HCOOH formed in phosphate buffers depending on the concentration of the phosphate buffer.[21] In Figure 7.3, we look more closely at the influence of the buffer capacity on

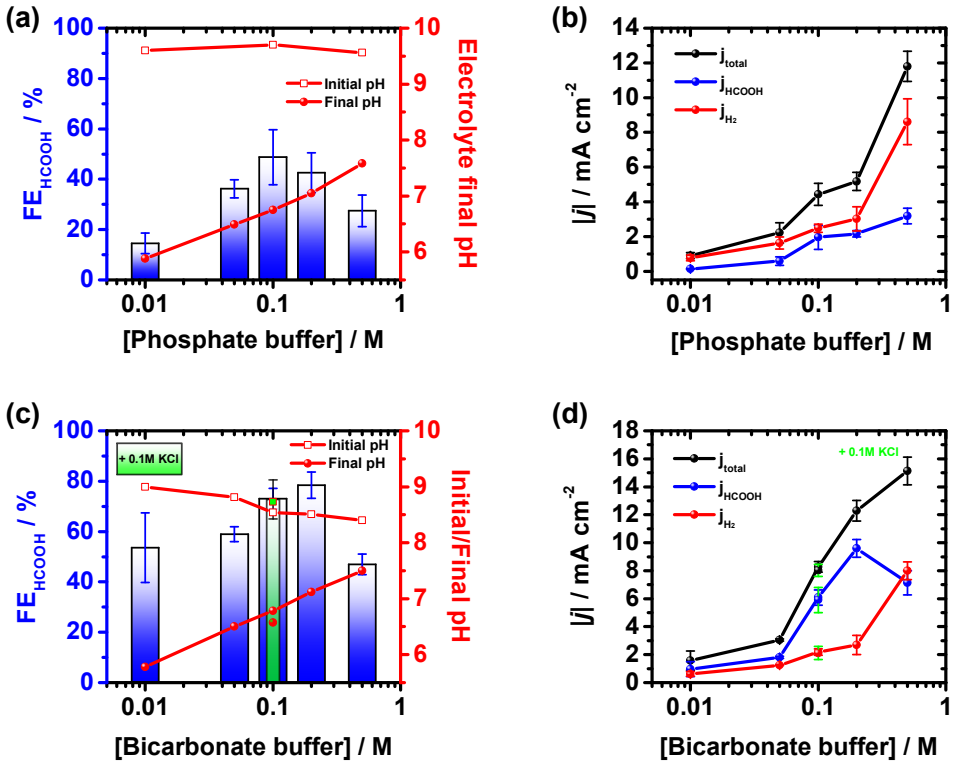


Figure 7.3 Faradaic efficiency toward HCOOH during 10 minute CO_2 reduction on immobilized InPP in (a) phosphate buffer and (c) bicarbonate buffer electrolytes with different buffering strenghts. Corresponding total current density and partial current densities for HCOOH and H_2 in (b) and (d).

the selectivity and activity of CO_2RR. We observe that an intermediate buffer capacity of 0.1 - 0.2 M leads to the highest CO_2RR selectivity in phosphate and bicarbonate buffers. This observation is different compared to the buffer capacity effect reported for copper electrodes,[6,7] which can be explained by the relatively simple product spectrum of our immobilized InPP compared to the product spectrum of copper, since the path toward either CH_4 or C_2H_4 on copper is known to be pH dependent.[26] Note that addition of 0.1 M KCl (in green in Figure 7.3c-d) does not lead to an improvement of the selectivity or activity. When studying the selectivity and activity as a function of time (Figure D.2), we find that a low buffer strength leads to an initial increase and eventually stable FE, while a high buffer strength is accompanied with a monotonic decrease in FE, and increase of hydrogen partial current (Figure D.2d), indicating the important role of local concentrations of protons and carbonaceous species. The presence of an optimum

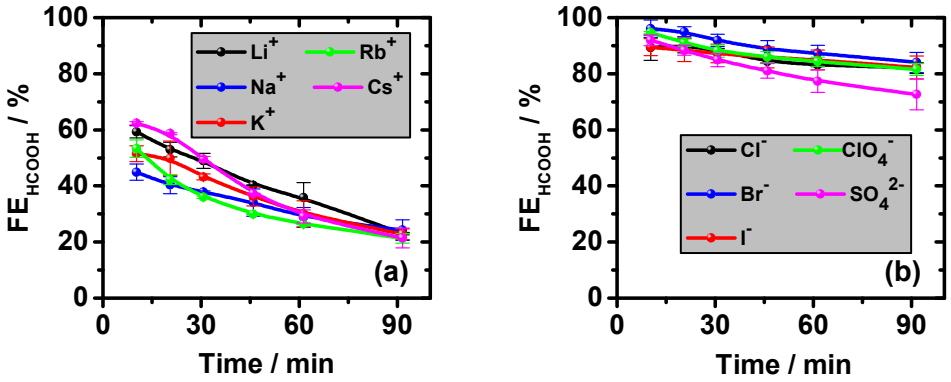


Figure 7.4 Faradaic efficiency toward HCOOH during CO_2 reduction on immobilized InPP in (a) phosphate buffer (pH 9.6) with 25 μM alkali cations in solution, and (b) 0.1 M KX electrolyte brought to pH $\approx$ 9.6, where X stands for different anions. Lines to guide the eye.

buffer capacity suggests at least two factors with opposite effects on the FE toward HCOOH. Moreover, these effects are likely to be time dependent, such as a stability issue or the settling of a new (local) equilibrium. A high buffer capacity reflects small local pH changes. The results indicate that small local pH changes negatively influence the stability and promote HER, while large pH changes suppress the HER and improve the stability. We believe that the enhanced rate of hydrogen evolution may affect the stability of the system, and a higher local pH is beneficial for high HCOOH selectivity. Differences in bulk pH after CO_2 saturation can be observed for the different buffer capacities shown in Figure 7.3a and c with red symbols. The trend of final pH between the different buffer solutions is as expected, and the possible correlation of final pH and FE is not similar to the trend observed before for the different buffer solution (higher final pH favors higher HCOOH selectivity). Deviation from this presumed correlation is observed for high final pH, which is similar to the KOH electrolyte as observed before. Therefore, we conclude that high selectivity toward HCOOH is not solely determined by the pH nor the buffer capacity, although both parameters seem to influence the faradaic efficiency toward HCOOH. Given the differences in selectivity and activity between the buffer electrolytes (Figure 7.1), we believe that also the pK_a of the buffer solution is important, influencing the CO_2 transport through the electrolyte, in agreement with recent work.[24]

In Figure 7.4a, we show that alkali cations do not significantly affect the CO_2 reduction performance on immobilized InPP, which is in contrast to the recent literature for heterogeneous electrocatalysts,[8–10,12] but in agreement with the different behavior of buffer capacity on CO_2RR for our system compared with heterogeneous electrocatalysts. Again, this could be due to the formation of only

HCOOH instead of C_1 and C_2 products, which is believed to be insensitive to differences in hydration number or pK_a value of the different cations as reported before.[11,12] Although Lewis acids such as Mg^{2+} were reported to positively impact CO_2RR under homogeneous conditions in DMF, we found that Mg^{2+} and Al^{3+} significantly worsen the selectivity toward HCOOH (Figure D.3). The promoting effect under homogeneous conditions in DMF is explained by electrophilic assistance, which helps the cleavage of C-O bonds.[16,17] Hence, it is reasonable that a similar effect is absent in our system, since the formation of HCOOH does not require C-O bond cleavage. Additionally, we observed a decrease in the electrolyte pH after addition of Al^{3+} ions, leading to promotion of HER and low FE toward HCOOH. These observations indicate the importance of the solvent, the reaction path (dominant product), and type of catalysis (homogeneous or heterogeneous) for the investigation of reaction- or process parameters on the CO_2RR selectivity and activity.

It was found in Figure 7.1 that KCl leads to higher FE compared to phosphate or borate buffer of similar pH. This enhancement could possibly be related to the presence of Cl^- ions in solution, since low buffer capacity does not lead to higher FE (Figure 7.3 and D.2a). Therefore, we systematically studied the influence of halide ions in solution. In Figure 7.4b, we compare the FE in electrolytes containing different anionic species brought to an initial pH of 9.6 by addition of KOH. Although no significant difference in selectivity is observed between the various anions, the FE is generally much higher compared to those observed earlier. An initial faradaic efficiency of 96 ± 3 % is even obtained in KBr electrolyte. Note, that there is no significant difference in the HCOOH selectivity between the typical adsorbing (halide and SO_4^{2-}) and non-adsorbing anions (ClO_4^-), which excludes an active site blockage effect.

7.4 Conclusions and Outlook

It can be concluded that the impact of electrolyte composition strongly depends on the type of catalysis, nature of the solvent and product distribution, and variations in the electrolyte composition can significantly affect the selectivity and activity of the CO_2RR. Although a cation or anion effect is absent, slight differences in the concentration or nature of ionic species in the electrolyte can affect the final pH, and consequently the performance of CO_2RR. The impact on the CO_2RR performance is believed to be a synergistic effect of various parameters such as pH after CO_2 saturation, buffering strength and pK_a of the electrolyte, which makes it difficult or even impossible to predict a priori the influence of a specific parameter on the CO_2RR performance.

The investigated system in this work, indium(III) protoporphyrin IX immobilized on pyrolytic graphite, behaves differently compared to homogeneous and heterogeneous electrocatalysts, since it does not show a typical cation nor anion effect for CO_2RR selectivity or reactivity. However, we show a strong influence of

the electrolyte composition and buffer strength on the selectivity of CO_2RR, where even the highest HCOOH selectivity for this system measured so far (FE $\approx 96 \pm 3$ %), is obtained in unbuffered electrolytes. Furthermore, the detachment of the porphyrin, leading to instability of the catalyst, is most likely associated to the low local pH and high hydrogen evolution activity.

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