Electrocatalytic CO2 reduction toward liquid fuels: on heterogeneous electrocatalysts and heterogenized molecular catalysts
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Effects of Substrate and Polymer encapsulation on CO₂ Electroreduction by Immobilized Indium(III) protoporphyrin

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Abstract

Heterogenization of molecular catalysts for CO$_2$ electroreduction has attracted significant research activity, due to the combined advantages of homogeneous and heterogeneous catalysts. In this work, we demonstrate the strong influence of the nature of the substrate on the selectivity and reactivity of electrocatalytic CO$_2$ reduction, as well as on the stability of the studied immobilized indium(III) protoporphyrin IX, for electrosynthesis of formic acid. Additionally, we investigate strategies to improve the CO$_2$ reduction by tuning chemical functionality of the substrate surface by means of electrochemical and plasma treatment, and by catalyst encapsulation in polymer membranes. We point out several underlying factors that affect the performance of electrocatalytic CO$_2$ reduction. The insights gained here, allow one to optimize heterogenized molecular systems for enhanced CO$_2$ electroreduction without modification of the catalyst itself.
6.1 Introduction

The electrocatalytic reduction of carbon dioxide (CO$_2$RR) is a potentially efficacious strategy to tackle the global energy concerns, particularly, to close the carbon cycle, and store renewable electrical energy in chemicals or fuels.[1] The latter is highly desired due to the intermittent character of renewable energy production. The last decades have experienced the discovery and development of various electrocatalysts, which all lead to a diversity of products with different selectivity and activity.[2–4] Besides heterogeneous CO$_2$ electrocatalysis using metal, metal alloy, or metal-derived, nanostructured electrocatalysts, molecular catalysis of CO$_2$ has shown interesting properties, and have undergone a striking development over the years.[5–8] Molecular catalysts are generally considered to yield high selectivity and activity, and can be designed in such a way to mimic enzymes used in nature to efficiently catalyze specific electrochemical reactions such as hydrogen evolution, water oxidation, carbon dioxide reduction, and oxygen reduction.[6,9] Although their stability and solubility in aqueous electrolytes and their poor robustness are often drawbacks, molecular catalysts are widely used to decipher mechanistic insight due to their well-known molecular structure and their efficiency. Hence, many studies have been performed on intrinsic catalyst properties such as the influence of the metal center[10–12] and ligands.[13–17] The focus herein will be on metalloporphyrins, a subgroup of molecular catalysts extensively used for CO$_2$RR research.[18,19] In previous work, we reported that cobalt(II) and indium(III) protoporphyrin IX (InPP) immobilized on pyrolytic graphite exhibit high selectivity toward carbon monoxide and formic acid, respectively.[12,20]

The usually poor solubility of molecular catalysts in aqueous media, and need for large amounts of catalyst related to homogeneous molecular catalysts, can be overcome by heterogenization. The molecular catalyst is immobilized on a conductive electrode, which we will refer to as "the substrate" in the remainder of this article. An additional advantage of immobilization of the catalyst is the more facile product separation, if utilized in a large-scale industrial process. Carbon materials are often employed as substrate owing to their relatively low cost, robustness and inert nature toward many (electro)chemical reactions. Examples are pyrolytic graphite, glassy carbon and more recently boron doped diamond, carbon nanotubes, and graphene.[21–23] Carbon materials exhibit a rich surface chemistry, and their surface functionalization has been proved to play an important role in their electrochemistry.[24] Studies by Morozan et al. and Rigsby et al. demonstrate the important influence of the carbon support of porphyrins on the selectivity of the oxygen reduction reaction.[22,25] Magdesieva et al. reported on activated carbon supports with different pore sizes for CO$_2$RR on various porphyrin and phthalocyanine complexes, leading to different selectivity.[26] However, little systematic or comparative work has been performed hitherto, to elucidate the intrinsic influence of the substrate or surface functionalization. The choice of a specific substrate is
often solely based on empirical considerations, which not necessarily is the optimal system.

Modification of electrodes started in the early '80s with several methods such as chemisorption or covalent attachment of species on the electrode surface, encapsulation of species in polymer films, or electropolymerization of monomers directly on the electrode.[27,28] More recently, Yaghi and coworkers developed a covalent organic framework of porphyrin building blocks, which showed promising results for CO$_2$RR.[29] An overview of various catalyst-modified electrodes for CO$_2$RR has been given by Sun et al.[30] From heterogeneous electrocatalysis of CO$_2$RR, it is known that the electrode morphology and (sub)surface structure significantly influence the activity and selectivity.[31–33] Moreover, the use of polymers has been shown to enhance CO$_2$RR efficiency on cobalt phthalocyanines.[34–36] In the field of heterogenized molecular catalysis of CO$_2$RR, the effects of such substrate modifications are still unexplored. The importance of chemical functionality on the adsorption and reactivity, as extensively discussed by McCreery,[24] is the inspiration of the idea that substrate modification may impact the reactivity, selectivity, and stability of CO$_2$RR. In a recent review, the importance of so-called secondary phenomena in molecular electrocatalysis have been highlighted.[37] It would be very attractive to be able to tailor the surface chemistry in such way, to enhance CO$_2$RR performance.

In this study we focus on extrinsic properties of the molecular catalyst, particularly related to the immobilization of the molecular catalyst. This work is a step toward a systematic investigation of chemical functionality of carbon substrates, and chemical environment for heterogenized molecular catalysts. Herein, we study InPP immobilized on different carbon materials, basal-plane pyrolytic graphite (PG), glassy carbon (GC) and boron doped diamond (BDD), and evince the important role of the substrate, its pretreatment and the use of polymer membranes for immobilization, on the CO$_2$RR performance. The current work demonstrates the improvement of CO$_2$RR performance on heterogenized indium(III) protoporphyrin IX by modifying the substrate, its chemical functionality, and chemical environment of the catalyst. The findings can function as a first step in trying to improve other heterogenized molecular systems as well.

### 6.2 Experimental

The electrochemical experiments were carried out with a potentiostat (IviumStat or CompactStat, Ivium Technologies), in a conventional three-electrode cell, where the working electrode (WE) and counter electrode (CE) compartments were separated by a nafion membrane (Nafion 115). Basal-plane pyrolytic graphite, glassy carbon, and boron doped diamond discs (5, 5, 10 mm diameter respectively) were used as WE. The counter and reference electrode (RE) were a platinum wire and a reversible hydrogen electrode respectively. For correct measurements versus the RHE scale, the luggin capillary and the RHE compartment were filled with CO$_2$ saturated electrolyte before CO$_2$ reduction. The electrolyte is 0.1 M phosphate buffer of pH
prepared with $K_2HPO_4$, $K_3PO_4$ and ultrapure water (Millipore MilliQ gradient A10 system, 18.2 MΩ·cm). The choice for this pH was based on the enhanced HCOOH selectivity observed previously.\cite{12} The reported current densities were always normalized by the geometric surface area of the WE, and in some cases additional normalization by the amount of active species was performed for correct comparison of the activity. The potentials were corrected for ohmic drop by the potentiostat during measurement. Generally, potentiostatic bulk electrolysis was performed at $E = -1.5$ V vs. RHE for 90 minutes, with manual collection of 100 µl samples at certain times, and analyzed by High Performance Liquid Chromatography. The reported concentrations of liquid products, or subsequently calculated faradaic efficiency (FE) are an average of 3 - 5 independent experiments with freshly prepared electrodes. Additionally, the data points for each experiment were obtained by the average of three injections of the same sample. The dominant contribution of the uncertainty in concentration/FE resulted from the different experiments. Additional experimental details can be found in Appendix C.

### 6.3 Results and Discussion

#### 6.3.1 Substrate effect

We compare the selectivity and activity for CO$_2$RR on InPP immobilized on PG, GC and BDD substrates. The immobilization procedure and amount of InPP dropcasted per cm$^2$ were kept the same for all the substrates (details in the SI). From the faradaic efficiency toward HCOOH, given in Figure 6.1a, it is observed that the substrate has a significant influence on the selectivity of CO$_2$RR on immobilized InPP. The PG substrate is the most selective toward HCOOH, and the GC substrate the least selective. These effects cannot be ascribed to the activity of the bare substrate as shown by control experiments in Figure C.17a, which show that bare PG, GC and BDD are not active for CO$_2$RR. In Figure 6.1b-d, the absolute total and partial current densities are shown for CO$_2$RR on the different substrates. For a correct comparison of the activity, the current density was also normalized by the real amount of InPP adsorbed on the substrate. As will be discussed in detail later, the electroactive coverage of InPP is not the same for the different substrates. It can be seen that there is an order of magnitude difference in $j_{\text{total}}$ and $j_{\text{HCOOH}}$ on PG compared to GC and BDD. Note that this difference is not associated to a difference in electrochemical active surface area (ECSA), as shown in Figure C.8(a). The fact that GC and BDD both perform worse compared to PG, indicates that the enhancement in CO$_2$RR selectivity and activity cannot be ascribed to either the high content of sp$^2$ or sp$^3$ carbon atoms present in respectively GC and BDD.

The results in Figure 6.1 are in line with the online mass spectrometry and online HPLC experiments, depicted in Figure 6.2a and b respectively, from which we confirm that significantly more H$_2$ is produced on InPP-GC, and significantly more HCOOH on InPP-PG. The CO$_2$ consumption on InPP-PG is also much
Figure 6.1 (a) Faradaic efficiency toward HCOOH, (b) absolute total current density, (c) absolute partial current density for HCOOH, and (d) absolute partial current density for H\(_2\) during CO\(_2\) reduction on immobilized InPP on different substrates in 0.1 M phosphate buffer of pH 9.6. Lines to guide the eye.

higher compared to the other substrates, in agreement with higher \(j_{total}\), and the higher HCOOH production rate observed on PG compared to the other substrates. Although difficult to quantify, the onset potential for H\(_2\) and HCOOH on InPP-BDD is at more negative potential compared to PG and GC, which is a general characteristic of BDD. Moreover, in Figure 6.2b we can observe differences in the peak potentials of HCOOH formation between the different substrates, which is related to the competition of the hydrogen evolution reaction (HER).

Besides a change in selectivity and activity, there is a clear difference in stability between the substrates, since a slight decrease is observed in \(j_{HCOOH}\) as a function of time on PG and GC, accompanied with an increase in \(j_{H_2}\). We define the relative FE with respect to the initial value (Equation 6.1) as a measure for the stability of the system. From a graph of this relative FE versus time (Figure 6.3a), we can compare experiments with different values of FE. A more horizontal trend indicates a higher stability as the FE does not decrease significantly in time.

\[
\frac{FE_t}{FE_{initial}} \times 100\% \tag{6.1}
\]

The tendency of the FE to decrease with time has been observed before, and was associated with the detachment of InPP from the surface or deactivation of the
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Figure 6.2 (a) Online Electrochemical Mass Spectrometry and (b) online HPLC during CO₂ reduction on immobilized InPP on different substrates in 0.1 M phosphate buffer of pH 9.6.

Porphyrin,[12] we have performed x-ray photoelectron spectroscopy on InPP-PG before and after electrolysis, as shown in Figure 6.3b. We observed that the indium content on the electrode, which is a measure of the actual amount of InPP adsorbed on PG, is substantially decreased after 10 minutes, with a negligible further decrease after 1 hour, which is in agreement with the decreasing trend of FE as a function of time. Additionally, we performed experiments under homogeneous conditions of InPP (Figure C.4), in which we do not observe a decrease in selectivity with time. Therefore we confirm that the destabilization of immobilized indium protoporphyrin is related to detachment from the surface. Moreover, the detachment from the surface takes place in the first 10 minutes of electrolysis. The adsorption of the porphyrin on the substrate is through noncovalent π-π interactions,[30,38,39] which is believed to be important for enhanced CO₂RR performance, and strongly dependent on the carbon substrate.

We believe that the substrate morphology plays an important role as evidenced by the higher CO₂ consumption observed with OLEMS, which can be explained by efficient mass transport effects due to the more porous structure of PG compared to GC or BDD (Figure C.8a), which may also suppress the HER. These observations are similar to mass transport effects recently reported for heterogeneous electrocatalysts, showing that the mesostructure can affect the selectivity and activity of
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**Figure 6.3** (a) Stability of immobilized InPP on different substrates (lines to guide the eye), (b) XPS spectra of InPP-PG electrodes before electrolysis and after electrolysis ($t = 10$ min and $t = 1$ h) with in the inset the indium content (at.%), (c) faradaic efficiency toward HCOOH (left axis) and partial current density for HCOOH (right axis) as a function of the amount InPP dropcasted on the different substrates (lines to guide the eye), and (d) indium content of the InPP immobilized on the substrates, as estimated from XPS, as a function of the amount InPP dropcasted (lines to guide the eye).

Additionally, a typical characteristic of GC is its poor permeability for gases, which likely affects the mass transport.[42] X-ray diffractometry and Raman spectroscopy of our substrates (Figure C.9a and C.10) indicate typical characteristics in agreement with the literature. PG and BDD exhibit sharp XRD peaks, and GC weak and broad peaks, indicating a high degree of crystallinity for PG and BDD, and a somewhat amorphous structure for GC.[43] The Raman spectra indicate the characteristic D- and G bands for sp$^2$ carbons in PG, and a specific peak associated to sp$^3$ carbon in BDD. The Raman bands for GC are weaker and less sharp, which indicate disorder of the graphite lattice for GC.[44,45] The low
activity and selectivity on GC may be associated with its poor crystallinity, as a high crystallinity infers enhanced charge transport, as observed in covalent organic frameworks.\textsuperscript{[29,46]} Recently, crystallinity has been shown to play an important role on the selectivity of CO\textsubscript{2}RR on copper phthalocyanine catalysts.\textsuperscript{[47]} However, high crystallinity alone is not sufficient for improved CO\textsubscript{2}RR catalysis, based on the significant differences in CO\textsubscript{2}RR performance between PG and BDD, which are both highly crystalline.

![Figure 6.4](image_url)  

**Figure 6.4** (a) Linear sweep voltammetry on immobilized InPP on different substrates in 0.1 M phosphate buffer of pH 9.6 under argon and CO\textsubscript{2} atmosphere, scan rate: 20 mV s\textsuperscript{-1} and (b) Online Electrochemical Mass Spectrometry measurement of hydrogen evolution on InPP immobilized on different substrates.

Apart from the substrate morphology and surface structure, a plausible explanation for the enhanced selectivity and activity on PG may be related to a difference in the effective amount of the porphyrin on the three substrates. As can be seen in Figure 6.3c, a difference in the amount of immobilized InPP on the substrate leads to a difference in activity and selectivity (details of the corresponding experiments are provided in Figures C.1-C.3). In case of PG this concentration effect is more pronounced, and in case of GC almost completely absent, which can be interpreted as a “InPP saturation limit” that is reached earlier for GC compared with PG. In other words, PG substrate can accommodate more catalyst compared to GC and BDD. These conclusions are in agreement with quantitative information obtained from XPS spectra of InPP immobilized on the different substrates (Figure C.12). We also varied the amount of InPP dropcasted on the different substrates and plotted the indium content as estimated by XPS vs. the amount dropcasted in Figure 6.3d. The vertical dashed lines indicate the InPP amounts used for the qualitative study shown in Figure 6.3c and C.1-C.3. It can be seen that the indium content is the highest for PG and the lowest for GC, which is in agreement with our conclusion that a PG substrate can accommodate more catalyst compared to GC. Furthermore, we used the indium content of InPP immobilized on different
substrates (PG, GC, BDD = 0.65, 0.49, 0.58) to normalize the activity to real amount of adsorbed InPP (Figure 6.1b-d).

Another cause of the improved CO$_2$RR selectivity may be a difference in HER activity between the substrates instead of solely an intrinsic substrate effect specifically related to CO$_2$RR. In Figure 6.4a, a comparison between the substrates for HER and CO$_2$RR is shown. The high overpotential for HER on the BDD substrate does not favor CO$_2$RR, since the CO$_2$RR onset potential is shifted toward more negative potentials, and the current is suppressed on InPP-BDD with CO$_2$ in solution. The HPLC results (Figure 6.2b) confirm the formation of HCOOH at more negative potentials on BDD compared to GC and PG. Under argon, where only hydrogen evolution takes place, the current density on InPP-GC is smaller compared to InPP-PG. However, as shown by OLEMS measurements in Figure 6.4b, more H$_2$ is produced on GC. Moreover, in the presence of CO$_2$, the onset potential is shifted positively for InPP-PG, but is almost unchanged for InPP-GC, which indicates a more efficient catalysis of CO$_2$RR on PG with respect to GC, in agreement with the online experiments in Figure 6.2. Consequently, the GC substrate is more active toward HER compared to PG. These results indicate that the competition between CO$_2$RR and HER strongly depends on the nature of the substrate, which in turn affects HCOOH selectivity.

In order to increase the impact and generality of our findings, we studied the substrate effect on protoporphyrins with Rh and Sn metal centers, which previously were found to produce HCOOH.$^{[12]}$ Although the HCOOH selectivity for these porphyrins is much lower than for InPP (which is an intrinsic catalytic effect), a similar trend can be observed for the different substrates as found for InPP (Figure C.5). Pyrolytic graphite substrate leads to the highest FE, while glassy carbon substrate is the least selective toward HCOOH.

The above results demonstrate the important influence of the substrate, which is believed to be the result of an interplay of several factors influencing the selectivity and reactivity of CO$_2$RR, such as morphology/mesostructure (and thereby optimized mass transport effects), crystallinity, electrostatic interaction with the molecular catalyst, and activity for HER.

### 6.3.2 Effect of substrate pretreatment

Besides the nature of the substrate, modification or treatment of the substrate surface offers a means to influence the CO$_2$ selectivity, reactivity, and stability. We investigated the influence of a cathodic and anodic electrochemical pretreatment ("Cat-PG" and "An-PG"), and a H$_2$ and O$_2$ plasma treatment ("H$_2$-PG" and "O$_2$-PG") of the PG substrate. In Figure 6.5, it is shown that O$_2$ plasma treatment increases the FE and $j_{HCOOH}$. These effects can be attributed to a change in chemical functionality as discussed later, instead of an increased surface area as evidenced by similar $C_{dl}$ before and after O$_2$ plasma treatment (Figure C.8b). Furthermore, the exposure time of O$_2$ plasma seems to play a role as shown in Figure C.6, since a mild O$_2$ plasma treatment (3 and 6 min. exposure) slightly
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![Figure 6.5](image)

Figure 6.5 (a) Faradaic efficiency toward HCOOH, (b) absolute total current density, (c) absolute partial current density for HCOOH, (d) absolute partial current density for H₂, (e) stability during CO₂ reduction on immobilized InPP on different pretreated PG substrates. Electrolyte: 0.1 M phosphate buffer of pH 9.6. Lines to guide the eye.

Improves CO₂RR, while a harsh O₂ plasma treatment (12 min exposure) worsens CO₂RR performance. In Figure 6.5(e), it is shown that O₂ plasma treatment has negligible influence on the stability. Anodization of PG leads to lower initial FE, but improves the stability dramatically. Moreover, both hydrogen treatments, cathodic and H₂ plasma, decrease the selectivity, reactivity and stability of CO₂RR significantly. Since H₂-PG has a lower Cdl and thus a smaller surface area (Figure C.8b), but a higher j_total, the observed changes in selectivity and reactivity do not result from a change in surface area of PG after H₂ plasma treatment.

The observed differences for the investigated pretreated PG substrates, highlight the role of oxygenated and hydrogenated functional groups of the substrate’s surface on the immobilization of InPP and subsequently on the CO₂RR. Our results imply that hydrogen functional groups on the PG surface strongly decrease CO₂RR selectivity, reactivity and stability, and oxygen functionalities increase CO₂RR performance. H₂ plasma consists of a large amount of H atoms, which reacts with surface oxides leading to C-H bonds and a decreased O/C ratio on the surface.[24,48] The chemisorbed hydrogen on the surface promotes HER with respect to CO₂RR, which is reflected in a decrease in FE and j_hcooh, and increase in j_H₂. On the other hand, O₂ plasma treatment increases the amount of oxygen functional groups (e.g. hydroxyl, carbonyl, carboxylate) on the surface, which generally leads to a more polar and hydrophilic surface and stronger adsorbate-substrate interaction.
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O$_2$ plasma treated PG shows an improvement in CO$_2$RR selectivity. A similar
influence of O$_2$ plasma treatment of the substrate has been reported before for the
oxygen reduction reaction.$^{[49]}$

On anodically treated PG we expected similar behavior as after O$_2$ plasma
treatment, due to the introduction of oxygenated species, but no improvement in
activity or selectivity has been observed. However, a remarkable increase in the
stability is observed. Based on blank voltammograms of the pretreated PG (Figure
C.7), there is a significant difference in An-PG compared to the untreated and
other pretreated PG electrodes. Application of strong anodic pretreatment causes
a destruction of the carbon surface, and formation of a thick graphite oxide layer,
which contains a high amount of anionic sites and interior void volume, leading to
high surface area, in agreement with the dramatic increase in $C_{dl}$ for An-PG in
Figure C.8b.$^{[24,50]}$ Complementary information was obtained by x-ray diffractometry,
Raman spectroscopy, and x-ray photoelectron spectroscopy. As shown in Figure
C.9b, the crystalline nature of PG remains intact upon electrochemical pretreatment.
However, anodization of PG leads to a significant increase in the Raman peak at
$\approx$ 1352 cm$^{-1}$, and a slight increase in the D' peak around 1620 cm$^{-1}$ (Figure
C.10b). The peak at 1352 cm$^{-1}$ is attributed to the presence of graphitic edges,
which increases in intensity upon anodic treatment as observed in our spectra, and
the peak at 1620 cm$^{-1}$ indicates delamination of graphitic planes. Formation of
graphite oxide increases the strain on the PG lattice, leading to fracturization.$^{[51]}$
In Figure C.11 the ratio of the D- and G band intensity for the different substrates
and pretreated PG is depicted, which clearly shows a high ratio of I$_D$/I$_G$ in case of
An-PG. Anodization of PG leads to an increase in the edge plane density. Note that
GC also exhibits a relatively high I$_D$/I$_G$, but showed a poor stability as seen before.
Therefore, we believe a high edge plane density in combination with high crystallinity
to be the reason for the strongly improved stability. The XPS spectra of the plasma-
and electrochemically treated pyrolytic graphite electrodes, shown in Figure C.13,
provide a quantitative basis for our conclusions about chemical functionality on
CO$_2$RR performance. The oxygen content is significantly higher on An-PG and
O$_2$-PG compared to untreated PG. Moreover, the H$_2$ plasma- and cathodically
treated PG exhibit less surface oxygenated species compared to untreated PG.
These results are in agreement with our interpretation of the CO$_2$RR results and
our Raman spectroscopy experiments.

6.3.3 Effect of polymer encapsulation

In addition to pretreating the substrate, another strategy aimed at improving
CO$_2$RR selectivity, reactivity and stability, is by incorporation of the porphyrin in
polymeric matrices. In this work, we compare the influence of didodecyldimethylam-
monium bromide (DDAB), nafion$^{\text{®}}$, poly(4-vinylpyridine) (P4VP), and poly(3,4-
ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS). Details about the
immobilization in these polymeric matrices are given in the SI. The concentration of
InPP in the polymer films, and the amount of polymer dropcasted per cm$^2$ surface
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Figure 6.6 (a) Faradaic efficiency toward HCOOH, (b) absolute total current density, (c) absolute partial current density for HCOOH (d) absolute partial current density for H₂, (e) stability during CO₂ reduction on immobilized InPP in different polymer membranes. Electrolyte: 0.1 M phosphate buffer of pH 9.6. Lines to guide the eye.

were always kept the same. As depicted in Figure 6.6, interesting differences are observed between the polymer membranes. Compared with polymer-free InPP (InPP-PG), encapsulation in DDAB, P4VP, and PEDOT:PSS shows enhanced selectivity and activity, whereas nafion negatively impacts the selectivity and activity. From Figure 6.6d it can be seen that the HER activity with P4VP is drastically decreased. A striking observation in Figure 6.6e is the enhanced stability when using P4VP or PEDOT:PSS compared to the other polymers. These results underscore the importance of the nature of the polymer as seen before for a modified bulk silver electrode.⁵² Enhanced CO₂RR performance by P4VP has been reported before for cobalt phthalocyanine, where the authors explain the observed effects by the presence of pyridine residues in the polymer, which influences the coordination to the catalyst.⁵³,⁵⁶ Although nafion coated catalysts are widely used for various electrocatalytic systems, negative effects of nafion on the catalytic activity have been observed previously.⁵³,⁵⁴

Differences in polymer-dispersed catalysts are generally associated with the introduction of a hydrophobic environment, leading to the suppression of the HER.⁵⁵ However, the differences in CO₂RR performance in our investigation are likely to be explained by the different chemical structures of the polymers (Figure C.14), leading to different substrate/adsorbate interactions. As can be seen in the blank CVs in Figure C.15, the typical InPP peaks are masked or
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shifted for nafion, P4VP and PEDOT:PSS. Changes in the voltammetric behavior
after immobilization of porphyrins in DDAB have been reported before, in which
the authors also suggest the possibility of porphyrin dimer formation in DDAB
vesicles.[55] The absence of InPP redox peaks in the investigated potential window
indicates a change in electrochemical behavior, but does not rule out the presence
of InPP on the surface since reasonable amounts of HCOOH are produced. The
CV of PEDOT:PSS coated PG shows a much larger double layer, which indicates
the strong influence of the polymer on the chemical environment near the electrode
surface. The polymers without InPP exhibit reasonable CO$_2$RR activity as can be
seen in Figure C.17b, where the same trend is observed as for InPP encapsulated
in the different polymers. A detailed investigation of the electrocatalytic activity
of polymers for CO$_2$RR is beyond the aim of this work. Nonetheless, it can be
concluded that the observed effects are partly due to the activity of the polymer
for CO$_2$RR, which is higher with P4VP and PEDOT:PSS. The pyridine group in
P4VP and aromatic moieties in PEDOT:PSS are assumed to play an important role
in this respect, since Dunwell et al. very recently reported CO$_2$RR toward HCOOH
mediated by pyridine.[56] The porphyrin exhibits a planar macrocycle with large
$\pi$-conjugation, which facilitates electrostatic interactions with the polymer. We
believe that the increased stability is a result of the presence of aromatic building
blocks as present in P4VP and PEDOT:PSS, which facilitates axial coordination to
the indium metal center by electron donation. This effect is known for pyridine or
imidazole ligands which are used for (covalently) anchoring catalysts to electrodes,
and are found to stabilize the coordination of CO$_2$.[34] This interaction is absent in
case of Nafion and DDAB, leading to a inferior stability compared to the polymer-
free InPP, P4VP and PEDOT:PSS. DDAB shows an increase in selectivity and
activity, which is associated with the suppression of the HER similar to previous
work.[52] The poor CO$_2$RR performance with nafion is tentatively ascribed to the
low mobility of the porphyrin in the polymer, and a disordered structure of the
nafion layer.[53,54] We performed electrochemical impedance spectroscopy on the
different polymer dispersed catalysts to investigate the kinetics of electron-transfer
processes (Figure C.16). As discussed in the SI, the charge transfer resistance
between the polymer films is in agreement with the observed activity in Figure 6.6b.
We conclude that the nature of the polymer affects the rate of electron transfer
during CO$_2$RR rather than mass transport of active species, leading to different
activity amongst the polymer films.

The results in the present work demonstrate that the hydrophobic environment,
induced by the polymer membrane in general, not always leads to suppression
of the HER activity and subsequent improvement of CO$_2$RR. Additional effects
related to the chemical structure, allowing for electrostatic interactions with the
porphyrin or activity towards CO$_2$RR by the polymer itself, play an important role.
Note that the current findings strongly depend on the (molecular) catalyst under
study, and one should be careful to generalize the observed polymer effects for other
electrocatalytic systems. Nonetheless, we emphasize the possible negative influence
of nafion on CO$_2$RR, as nafion is very often used to immobilize catalysts, or as binder in the preparation of ink containing nanoparticulate electrocatalysts.

6.4 Conclusions

This work has shown the importance of the nature of the substrate for immobilized indium(III) protoporphyrin IX for CO$_2$RR toward formic acid. For this particular system, a pyrolytic graphite substrate outperforms glassy carbon and boron doped diamond in terms of CO$_2$RR selectivity and reactivity, while boron doped diamond shows the best stability. The enhanced activity and selectivity of PG are assigned to a combination of different factors. First, to a more porous surface structure, leading to efficient mass transport. Furthermore, to an optimal interaction between substrate and InPP, and a favorably low HER activity.

We have investigated two strategies to improve or alter the selectivity, reactivity, and stability of CO$_2$RR. Pretreatment of the substrate before catalyst immobilization, and immobilization in polymeric matrices have shown to be practical tools to fine-tune CO$_2$ reduction performance. Hydrogenated functional groups on the surface decrease the selectivity, activity, and stability, while (mild) oxygen functionalization positively influences the CO$_2$ reduction performance. Anodization of the graphite surface substantially increases the stability, which is believed to be related to the thick graphite oxide layer containing high edge plane density. Both P4VP and PEDOT:PSS, increase the stability, which is believed to be due to axial coordination of their aromatic moieties to the indium metal center. DDAB, P4VP and PEDOT:PSS improve the performance of CO$_2$RR, while nafion impacts CO$_2$RR negatively. These strategies are assumed to be applicable to similar macrocyclic catalysts immobilized on carbon materials.

It should be noted that the CO$_2$RR performance is often a trade-off between selectivity, activity, and stability, each of which can be modified by substrate pretreatment and catalyst encapsulation in polymers. Although complete mechanistic insight in the pretreatment- and polymer effects is still missing, the results obtained here, may help to design heterogenized molecular catalytic systems for CO$_2$ reduction with specifically optimized properties. Other molecular catalysts may behave differently, hence one should be careful generalizing the results obtained in this study. However, it is very likely that the substrate, its pretreatment, and catalyst dispersion in polymers will have an influence on CO$_2$RR performance, and the insight obtained herein may be used as starting point for further optimization of the system.

6.5 References

Chapter 6. Effects of Substrate and Polymer encapsulation on CO₂ Electroreduction by Immobilized Indium(III) protoporphyrin


Chapter 6. Effects of Substrate and Polymer encapsulation on CO$_2$
Electroreduction by Immobilized Indium(III) protoporphyrin


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