Polymers with Intrinsic Microporosity (PIMs) for targeted CO2 reduction to ethylene

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# Abstract

CO2 reduction offers an attractive alternative green synthetic route for ethylene, especially where CO2 could be sourced from industrial exhausts and in combination with green power sources. However, practical applications are currently limited due to the unfortunately low selectivity of cathode materials towards ethylene. This work uses polymers with intrinsic microporosity (PIMs) to improve the performance of copper gas diffusion electrodes for CO2 reduction to ethylene. We report an improved selectivity and activity towards ethylene with the addition of a thin PIMs layer, which is seen as improved Faradaic efficiency, increased stability and a shift in the reduction to lower overpotential. This improvement is highly dependent on the thickness of the added polymer layer, with too thick a layer having a detrimental impact on the hydrophobicity of the gas diffusion layer. With a compromise in loading, PIMs can be used to enhance the activity and selectivity of catalysts for targeted CO2 reduction to ethylene.

# Keywords

Carbon dioxide; ethylene; electrochemistry; polymers with intrinsic microporosity; gas diffusion electrode; triphasic interface

# Introduction

The CO2 reduction reaction (CO2RR) is a rapidly expanding area of environmental chemistry, as it offers solutions to a number of concerns around CO2 chemistry (Pletcher, 2015). The reduction of CO2 towards carbon fuels such as methane provides an energy storage solution for intermittent green energy providers such as solar and wind (Lin et al., 2015; Gao et al., 2016; Liu et al., 2016). Alternatively, the target of CO2 reduction may be an industrially relevant compound such as CO (Medina-Ramos et al., 2015; Rasul et al., 2015; Rosen et al., 2015; Verdaguer-Casadevall et al., 2015; Feaster et al., 2017) or C2H4 (Schouten et al., 2012; Ogura, 2013; Varela et al., 2016; Dinh et al., 2018; Hoang et al., 2018). In all cases, the combination of CO2 as a feedstock chemical with green power sources offers a synthetic route with a net decrease in total CO2 concentration. C2H4 in particular has received significant interest thanks to its use in the synthesis of polymers that would normally be sourced from fossil fuels.

Currently, the electrosynthesis of C2H4 from CO2 is hindered by a relatively low selectivity, with significant quantities of CO, H2 or CH4 usually being the dominant side-products (Yano et al., 2004; Tang et al., 2012). Additional problems appear when running these systems at high current densities, as increased overpotentials drive the reduction of water, resulting in a product mixture containing even more H2 (Gattrell et al., 2006; Varela et al., 2015).

CO2 + 2e– + 2H+ → CO + H2O *E*0 = –0.103 V vs SHE (1)  
CO2 + 8e– + 8H+ → CH4 + 2H2O *E*0 = 0.169 V vs SHE (2)  
2CO2 + 12e– + 12H+ → C2H4 + 4H2O *E*0 = 0.079 V vs SHE (3)  
2H+ + 2e– → H2 *E*0 = 0.000 V vs SHE (4)

Fundamentally, the challenges associated with reducing CO2 to C2H4 come from the overlap of standard potential with that of hydrogen evolution, the requirement of twelve electron transfers, and the need for CO2 adsorption to facilitate the formation of carbon-carbon bonds (Bushuyev et al., 2018). In fact, C2H4 has been reported to have the highest capital operating costs of the possible CO2RR products, due to the large current and large CO2 feedstock needed (Jouny et al., 2018). These limitations are reflected in the restricted market-readiness of present CO2RR technologies. Associated costs will come from concentration of CO2 into the feed gas, performance of the electrolysis, and purification/separation of the outflow gas (Pletcher, 2015).

Concentrating the feed gas can be simplified by integrating the reactor with an existing source of concentrated CO2 such as power or fermentation plants, and electrolysis can be hyphenated with green energy sources to reduce associated costs (Bui et al., 2018). Further costs can be offset by coupling CO2 reduction at the cathode with a second industrially relevant oxidation at the anode (Na et al., 2019). Most efforts towards making CO2 reduction to C2H4 economically feasible are therefore focused on giving high selectivity at large current density to minimise product separation costs.

A number of collaborative research projects are developing technologies for CO2 reduction to value added projects, most of which are working in the range of TRL 3 to 6 (Sánchez et al., 2019). A handful of up-scaled reactors have been demonstrated for two-electron CO (Kaczur et al., 2018; Endrődi et al., 2019), or syn-gas production (Sánchez et al., 2019) but as yet not for C2 reduction products. As such, an improved catalytic performance (e.g. 300 mA cm-2 at 0.5 V overpotential with 70% Faradaic efficiency) is needed before higher order carbon dioxide reduction can be economically viable (Jouny et al., 2018).

Much research has therefore been dedicated to designing reaction systems that can favour C2H4. So far, copper and copper alloy electrodes have dominated the literature, with simple copper electrodes already producing C2H4 as the main electrochemical reduction product (Takahashi et al., 2002; Hori et al., 2003). Recent works have further improved on selectivity either by manipulation of the catalyst material (Yano et al., 2004; Ogura et al., 2005),surface structure (Yano et al., 2007; Tang et al., 2012; Dinh et al., 2018; Hoang et al., 2018), or electrolyte (Ogura et al., 2010; Varela et al., 2016; König et al., 2019). As well as producing C2H4 from CO2 reduction, these materials also have to either supress water reduction, or lower the required overpotential for C2H4 electrosynthesis, in order to inhibit the simultaneous formation of H2.

A number of works have also demonstrated an increase in the current density for CO2 reduction by changing the reaction vessel. CO2 electrochemistry in general is hindered by low CO2 solubility (Yano et al., 2002). The highest current densities are invariably produced with gas diffusion electrodes (GDEs), which remove this problem by flowing CO2 in the gas phase through a porous electrode (Yano et al., 2004; Ogura et al., 2005). CO2 then reacts at the gas-liquid interface soon after it dissolves, so the mass transport rate is kept high without being hindered by the solution solubility. Additional improvements have been made by taking steps to improve the hydrophobicity of the electrodes, so that the electrode does not become saturated with solution and CO2 diffusion is uninhibited within the gas phase (Dinh et al., 2018).

Recently, polymers with intrinsic microporosity (PIMs) have been used to enhance the performance of electrochemical systems such as the oxygen reduction reaction (ORR) (Madrid et al., 2019). These polymers assemble on the surface of catalysts, resulting in a highly microporous structure capable of storing reactive gases at the electrode surface in a triphasic environment (Marken et al., 2019). This prevents the formation of bubbles at the catalyst surface, which would block active sites, and has been shown to improve the apparent activity of the gas itself to electrochemical consumption. Here, we use the same procedure to modify the surface of copper nanoparticles at gas diffusion electrodes in order to enhance the catalyst performance both in terms of the rate of CO2RR and selectivity towards C2H4.

# Materials and methods

## 2.1 Electrode preparation

The Cu film (100 nm thickness) was deposited on a carbon GDE (Freudenberg H23C2 carbon paper, 14 cm x 10 cm) by direct current magnetron sputtering (dcMS) from a metallic Cu (purity 99.99%) target in an Ar (purity 99.99%) atmosphere. The deposition was performed using a vacuum coater G500M/2 (Sidrabe). Before the film deposition, the chamber (≈ 0.1 m3) was pumped down to base pressure below 1.3 × 10–5 mbar by a HiPace 1800 turbo-molecular pump (Pfeiffer) backed with a rotary pump. The pumping speed was altered by a throttle valve to set the working pressure of 2.6 × 10–3 mbar when the Ar flow of 20 sccm was introduced. An ION’X® planar, balanced magnetron (Thin Film Consulting) with target dimensions 100 mm × 200 mm × 9 mm was used. The power was supplied by a power unit SIP2000USB-10-500-D (Melec) operating in a constant DC mode at a power of 200 W (1 W cm–2). The negative voltage was supplied to the magnetron cathode against a grounded anode. The substrate was not heated intentionally during the deposition process and the distance between the target and the substrate was approximately 19 cm (the substrate facing the target axis). The deposition time was 5 min to obtain a 100 nm thick film (20 nm min–1). All analyses in this work were carried out by cutting 1.5 x 1.5 cm samples from the same 14 cm x 10 cm GDE.

The PIM used in this work is designated as PIM-EA-TB, signifying its identifiable component structures ethanoanthracene (EA) and Tröger’s base (TB). The detailed synthetic route to PIM-EA-TB has previously been published (Carta et al., 2013). The solid PIM was dissolved in chloroform to give a 1 mg mL–1 solution, which was drop cast on to the copper GDEs to give the desired loadings. After the chloroform evaporates a microporous film of PIM-EA-TB remains on the surface of the copper particles (Fig. 1).



**Figure 1.** Schematic diagram of the copper coated GDE with the added PIMs layer. CO2 flows through the back of the carbon layer. The electrolyte is able to permeate the PIMs layer, so the CO2 will dissolve inside the hydrated PIMs, creating the triphasic interface. The CO2 is reduced at the copper catalyst to C2H4, which re-enters the gas phase for collection. Some CO2 reduction to other carbon products, and water reduction to H2 will also be seen. The red inset shows the structure of PIM-EA-TB used in this work.

## 2.2 Contact angle measurements

All samples were dried under air before the analysis. The water contact angle measurements were acquired using the Contact Angle System (OCA, dataphysics) goniometer. 30 μL droplets of distilled water were transferred onto each Cu GDE using a syringe pump. The water contact angles were measured at ambient temperature and fit to the Young-Laplace equation. Measurements were carried out 3 times on different areas of the samples to check the repeatability.

## 2.3 SEM imaging

All SEM images were obtained using a Hitachi SU3500 variable pressure scanning electron microscope equipped with XEDS (Oxford, Inca, Silicon drift detector). Topographic information was obtained by collecting the secondary electron signal produced from the specimen itself while elemental composition information was explored via detection of back-scattered electrons stemming from the incident beam and X-ray emissions. The samples were immobilized onto the SEM sample stub using double-sided carbon tape. The beam strength was 20 kV and a spot size of 50 nm was used.

## 2.4 Ethylene electrosynthesis and detection

The copper GDE was loaded into a glass cell, which was fabricated in house. The aperture of the cell revealed a 1 cm2 area of the deposited copper to the electrolyte. A PTFE gasket was placed in front of the GDE to help prevent leaks, with a stainless steel flow field at the back of the assembly, which also functions as the current collector. The cell was then filled with 1 M KOH (85%, Fisher) as the electrolyte, and was loaded with a Pt mesh counter electrode (CE) and Ag/AgCl reference electrode (RE) (IJ Cambria). CO2 (99.995%, BOC) was flowed at 0.1 L min-1 over the back of the GDE via the flow field (Fig. 2)



**Figure 2.** Schematic diagram for the gas diffusion electrode cell used in this work. The reference electrode (RE) is introduced into the cell via a Luggin capillary to reduce the IR drop. The counter electrode (CE) is a Pt mesh. The working electrode (WE) is a copper coated, carbon gas diffusion electrode. The cell volume is around 75 mL. A 1 cm2 active area is isolated using a PTFE gasket. The copper-coated side faces the electrolyte, and the stainless steel flow field is clamped in place behind. The flow field has a tight spiral design with a 1.5 mm depth to maximise the interaction of the CO2 with the copper catalyst. The flow field also acted as the current collector.

Electrochemical experiments were performed using an Autolab potentiostat (Metrohm PGSTAT204) with 10 A current booster. Data were collected using Nova 2.1. Gas was collected from the flow field outlet in 1 L Teldar® gas sampling bags. Reduction products were then analysed ex situ using gas chromatography (GC) using a Shimadzu GC 2030 with a Porapak Q 80/100 column. CO was detected using a thermal conductivity detector, CH4 and C2H4 were detected using a flame ionisation detector. The gas chromatograph was calibrated using gas mixtures of known concentrations of CO, CH4 and C2H4 (SIP Analytical). The Faradaic efficiencies (%FE) for CO, CH4 and C2H4 are defined as the percentage of passed charge that produces the specified product, which were calculated using Eq. 5

|  |  |
| --- | --- |
|  | (5) |

where *n* is the number of electrons, *F* is Faraday’s constant, *c* is the concentration in ppm, *V* is the volume of the analysed gas sample, *V*m is the molar volume of the gas, and *Q* is the charge passed while the gas sample was collected.

# Results

## 3.1 CO2 reduction to ethylene

Copper GDEs with 0, 0.01, 0.05 and 0.1 mg cm-2 PIMs were analysed for their CO2 reduction performance using linear sweep voltammetry (LSV) in 1 M KOH. KOH is chosen, as the high pH and strongly adsorbing OH– ions hinder hydrogen evolution, which results in an improved selectivity towards CO2 reduction products (Dinh et al., 2018). Electrodes were biased 200 mV negative of the open circuit potential (OCP) and then swept at 1 mV min–1 until –300 mA cm-2 was reached as a cut-off value (Fig 3A). The presence of the PIMs layer has a sizeable impact on the position of the reduction wave, with all loadings shifting the wave to lower overpotentials with respect to the bare copper GDE, indicating a more kinetically facile CO2RR process.

The reported current in Fig 3A is a combination of CO2 reduction to all possible products (Eqs. 1-3) along with H2O reduction to H2 (Eq. 4). In order to view the impact of the PIMs specifically on the formation of C2H4, GC measurements were taken at 50 mV intervals along the reduction wave. By relating the %FE of C2H4 () to the total current passed (), it is possible to express the LSV in terms of the current passed due to the reduction of CO2 specifically to C2H4 (, Fig 3B).

|  |  |
| --- | --- |
|  | (6) |

Importantly, the LSV for shows the same trend, where the PIMs layer results in a sizable shift in the reduction wave to lower overpotentials. This indicates that the PIMs are enhancing the kinetics of the CO2RR specifically to C2H4 rather than just enhancing the overall CO2 reduction to other products. This is confirmed by the change in the Tafel slope from –133 to –88 mV dec–1 with the addition of 0.01 mg cm–2 PIMs (Fig. 3C), where a smaller value indicates that less potential energy is required to give an order of magnitude increase in reaction rate. Isolating also reveals that the passed current towards forming C2H4 is increased with the presence of the PIMs layer. This is reinforced by looking at the change in the during the sweep, where the electrode with 0.01 mg cm–2 PIMs approaches 50% at –0.63 V *vs.* RHE, compared to around 20% for the bare electrode at –0.78 V *vs.* RHE (Fig 3D).

**Table 1.** Faradaic efficiency towards CO () CH4 () and C2H4 () of a number of leading catalyst materials for the electrochemical synthesis of C2H4 from CO2 electrochemical reduction. Table is sorted by decreasing order of Faradaic efficiency. A lower efficiency at higher current density may produce more C2H4, but would be more energetically wasteful.

The impact of the PIMs coating on both the position of the wave and the maximum and is important, as this indicates that the PIMs can enhance both the activity of the catalyst towards the CO2RR selectivity of the CO2RR towards C2H4. At this point, it is not clear whether the hindering of water reduction or the activation of CO2 is responsible for the sizeable improvement in performance. Examples exist in the literature where the PIMs are able to activate gaseous reactants (Madrid et al., 2019) and where hindering water reduction can shift the CO2RR to lower overpotentials (Dinh et al., 2018), as is seen here. A more complete picture of the chemistry within the PIMs coated GDE is needed before the mode of enhancement can be defined. A comparison of the performance of the PIMs and non-PIMs coated GDE to a number leading literature examples is given in Table 1.

A recorded of 45.5% at –67.4 mA cm–2 compares favourably with many examples in the literature. However, it is worth noting that some recent alternative electrode designs have been able to achieve higher efficiencies at higher current densities than are reported here, through new alloy catalysts or specially designed GDE interfaces. The key feature of this work is how the PIMs layer is able to enhance the %FE of a relatively simple GDE architecture. This is highlighted in Table 1, as the PIMs coating takes our Cu GDE from the bottom of the table up the fifth position, with no other modifications being made. This opens the potential to further enhance specifically engineered catalysts with already high %FE, to push leading catalysts to even greater selectivity.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Material |  |  |  | *j* / mA cm–2 | Reference |
| Graphite/C nanoparticles/Cu/PTFE | 2.5 | 0 | 70 | –100 | (Dinh et al., 2018) |
| Cu-Ag wire | 6.5 | 1.6 | 55.2 | –310 | (Hoang et al., 2018) |
| Cu nanocubes | 24 | 0 | 51 | –160 | (Wang et al., 2019) |
| Hydrophobic Cu dendrites | 3 | 7 | 56 | –30 | (Wakerley et al., 2019) |
| Cu with PIM-EA-TB in this study | 4.4 | 5.8 | 45.5 | –67.4 | This work |
| Metal organic framework Cu clusters | 24 | 0.4 | 45 | –262 | (Nam et al., 2018) |
| Oxide derived Cu | 0.6 | 2.8 | 43.1 | –13 | (Lum and Ager, 2019) |
| CuZn alloy | 14.1 | 0 | 33.3 | –6.1 | (Feng et al., 2018) |
| Thermally annealed Cu nanowires | 18.9 | 0 | 27.0 | –300 | (Zhang et al., 2019) |
| Cu nanoparticles | 31.1 | 0.1 | 24.4 | –300 | (Romero Cuellar et al., 2019) |
| Cu without PIM-EA-TB in this study | 2.5 | 3.3 | 18.6 | –76.1 | This work |

Also detected at these potentials were smaller amounts of CO and CH4, with all GDEs giving %FE < 5% of these species at the corresponding potentials, regardless of the PIMs coating used. This is fairly typical of the high selectivity towards C2 carbon products of copper catalysts at high overpotentials (Vasileff et al., 2018). Although not explicitly detected in this experimental design, the remaining Faradaic efficiency can likely be attributed to water reduction to hydrogen, since other carbon dioxide reduction products such as ethane or formate typically show lower Faradaic efficiencies than CO and CH4 under these conditions (Ogura, 2013). The decrease in at *E* < –0.65 V *vs*. RHE corresponds to an increased rate of H2 production, since water reduction is not hindered by the same mass transport limitations as CO2 reduction at the GDE surface. This highlights why a number of works have focused on hindering the hydrogen evolution reaction to enhance carbon dioxide reduction selectivity at high current densities (Ogura et al., 2010; Ooka et al., 2017; Dinh et al., 2018).



**Figure 3. A.** Linear sweep voltammogram (LSV) in 1 M KOH at 1 mV min-1 for CO2 reduction at a copper GDE with 0 (black), 0.01 (red), 0.05 (green) and 0.1 mg cm–2 (blue) PIMs, loaded by drop casting in chloroform. **B.** Extracted current densities due to the reduction of CO2 specifically to C2H4 (), calculated using Eq. 6. **C.** Calculated Tafel slopes for all electrodes. Linear fit was performed from the first potential that produces C2H4 over 200 mV. A shallower gradient indicates the reaction is kinetically more facile. **D.** during the recorded LSV. In all cases, the performance of the electrodes follows 0.01 > 0.05 > 0.1 > 0 mg cm–2. Connecting lines between data points in B and D are intended as a visual aid only.

Interestingly, the shift in the position of the CO2 reduction wave is not linearly dependent on the loading of PIMs on the catalyst surface. A small loading of 0.01 mg cm–2 results in a greatly improved performance for C2H4 production. However, increasing this loading by an order of magnitude results in an intermediate performance, with the reduction wave sitting in between that of the thin PIMs coating and the bare electrode. Small doses of the PIMs appear to provide the desired increase in catalyst activity, but further increasing the loading results in an increasingly muted effect. This suggests that the PIMs coating are having an impact on additional properties outside of the kinetics of the CO2RR or the rate of hydrogen evolution.

## 3.2 Stability of the electrochemical response

The stability of the GDEs with and without the PIMs coating was probed by biasing the electrode at -0.9 V vs RHE in 1 M KOH and reducing CO2 for 6 hours. was evaluated every 30 mins to track the change in the electrode activity (Fig. 4). As with the LSV, the presence of the PIMs layer has a sizeable impact on the stability of the GDEs.



**Figure 4. A.** for copper GDEs biased at -0.9 V *vs.* RHE in 1 M KOH, recorded with 0 (black), 0.01 (red), 0.05 (green) and 0.1 mg cm–2 (blue) PIMs on the electrode surface. The maximum time where C2H4 was still detected follows 0.01 > 0.05 > 0 > 0.1 mg cm–2. Connecting lines between data points are intended as a visual aid only. **B.** 200 mV s–1 cyclic voltammograms (CVs) recorded before (black) and after (red) the 6-hour reduction experiment in A, recorded with 0 mg cm–2 PIMs on the electrode surface. The characteristic copper peaks can still be seen after the 6-hour reduction, indicating that the copper is still present. **C.** SEM images of the Cu GDE with 0 mg cm–2 PIMs recorded before (left) and after (right) the 6-hour reduction experiment in A. Images of the electrode surface are at 1000× (top) and 10,000× (bottom) magnification. The electrode structure can be seen to be largely unchanged, with Cu particles still present.

The stability of the all of the GDEs was relatively poor regardless of the loading, with the bare electrode ceasing to produce detectable quantities of C2H4 after 3 hours. As was seen in Fig. 3, the impact of the PIMs on stability is not linear; a small loading of 0.01 mg cm–2 increased the stability whereas a larger loading of 0.1 mg cm–2 PIMs reduced the stability.

Cyclic voltammetry (CV) recorded before and after the 6-hour reduction period (Fig. 4B) show that the copper is still present on the GDE after use, so the activity loss cannot be explained by a loss in catalyst material. The presence of the copper was confirmed using SEM (Fig. 4C), and the clear copper colour of the GDE could still be seen by eye as well. The CVs also show a large increase in the charging current, indicating an increase in the electrochemically active area of the GDE. This could be explained by a flooding of the GDE, which results in the carbon support coming into contact with the electrolyte. This would explain the loss in CO2RR activity, as a flooded GDE forces CO2 mass transport into the liquid phase, which greatly slows the rate of reaction due to a decreased diffusion rate and poor CO2 solubility. The electrochemically active carbon also greatly increases the number of active sites for water reduction, whilst being poorly active for the CO2RR to C2H4, which reduces the proportion of the current density dedicated to the CO2RR.

## 3.3 Impact of PIMs on hydrophobicity

The non-linear dependence of the GDE activity, selectivity and stability on the applied PIMs loading indicates that the PIMs are affecting properties of the GDE outside of the electrochemistry. The increased charging current in Fig 4B suggested that the stability loss is due to a flooding of the GDE with electrolyte. In order to hinder the flooding of the carbon, commercial GDEs are fabricated with hydrophobic components within the carbon structure. A series of contact angle measurements were performed on the GDE with all of the tested PIMs loadings, to see how the PIMs affect the hydrophobicity of the GDE surface. The electrodes were tested once more after the 6-hour potentiostatic CO2 reduction in order to track the change in hydrophobicity after extended use (Fig. 5).



**Figure 5.** Contact angle measurements on copper GDEs with varying PIMs loadings, recorded before (black) and after (red) the 6-hour potentiostatic CO2 reduction. A larger contact angle indicates a more hydrophobic surface. Error bars are one standard deviation (*n* = 6). Blue data points show the percentage decrease in contact angle after the 6-hour reduction. PIMs coated electrodes were substantially more resistant to changes in hydrophobicity due to prolonged operation, although greater loading of the PIMs also decreased the starting contact angle.

The impact of the PIMs on the hydrophobicity needs to be discussed separately, firstly in terms of the impact on the starting hydrophobicity of the PIMs coated electrodes, and secondly in terms of the change in hydrophobicity after a period of extended use. Looking at the initial hydrophobicity (Fig. 5, black points), an increase in PIMs loading causes a stepwise decrease in hydrophobicity. Dropcasting the PIMs in chloroform allows the PIMs to permeate the GDE structure. This thicker PIMs layer can become more hydrated, drawing water into the GDE and decreasing the hydrophobicity. Although the impact of the 0.01 mg cm-2 loading is minimal, the larger 0.1 mg cm-2 loading reduces the starting contact angle by 26% with respect to the bare GDE, representing a sizeable decrease in the hydrophobicity of the surface. Interestingly, although the PIMs decrease the hydrophobicity of the GDE surface, they create a surface that is more stable to changes in the hydrophobicity after extended operation (Fig. 5, blue points).

Taking the percentage difference between the contact angle before and after the 6-hour reduction, PIMs coated samples show a relatively small loss in contact angle of around 25%, compared to a much larger 63% for the bare sample. It seems that the PIMs can be rapidly hydrated, giving the initial decrease in hydrophobicity, but give a very slow rate of water loss into the GDE, which acts as a barrier to GDE flooding. A compromise PIMs loading would therefore be able to hinder GDE flooding without sizably wetting the internal GDE structure.

# Discussion

The complicated relationship between the PIMs loading and the CO2 reduction properties highlights the impact of the PIMs on multiple properties of the GDE. The addition of 0.01 mg cm-2 PIMs to the copper electrodes reduced the onset potential, decreased the Tafel slope, and increased the maximum . This is in agreement with previous work where PIMs coated electrodes shifted the oxygen reduction reaction peak to less negative potentials (Madrid et al., 2019). The improved selectivity and activity of the CO2RR towards C2H4 could come from either an enhancement of the CO2RR process to give more selective electrochemistry to C2H4, or from the hindrance of water reduction, freeing active sites for CO2 adsorption and increasing the proportion of the charge that goes towards the CO2RR.

The change in contact angle with the addition of 0.01 mg cm-2 is very small, so this great improvement in performance cannot be ascribed to differences in the hydration of the copper layer. It is also worth considering the impact that the PIMs will have on water reduction, since this involves gaseous H2 as the product. It is likely that the triphasic environment within the PIMs will be made up certain quantities of both CO2 and H2, with CO2 coming from the gas phase and H2 from water reduction at the catalyst surface. It may seem possible that the increased H2 concentration within the PIMs could disrupt the water reduction equilibrium to reduce the rate of reaction. However, since the concentration of water is always significantly higher than that of H2 due to its low solubility, it is likely that the PIMs will have only a negligible impact on the rate of water reduction.

Instead, it seems likely that the positive impact of the PIMs on CO2 reduction stems from the triphasic interphase formed by the deposited PIMs. CO2 can be stored inside the porous PIM structure close to the electrode surface, which facilitates reduction at the copper catalyst. The triphasic interface may also act to prevent CO2RR intermediates, specifically CO, from being released from the electrode before further reduction to C2H4 can be achieved. A number of works have shown that CO is a key intermediate of CO2RR to C2H4 (Schouten et al., 2012; Kortlever et al., 2015), so much so that the CO adsorption energy can be used as a descriptor for CO2RR selectivity to specific products (Liu et al., 2017; Hussain et al., 2018). It is also possible to use CO as a starting material for C2H4 electrochemical synthesis (Romero Cuellar et al., 2019). Any CO released by the catalyst could become trapped in the PIMs triphasic interface and then further reduced, giving an improved C2H4 and less product loss as CO.

The benefits of the PIMs for CO2 reduction at GDEs seem to require a compromise against the change in hydrophobicity that comes with greater loadings. The nature of the triphasic interface means that the PIMs layer is hydrated, which can draw water into the GDE and give a less hydrophobic surface. Reduced hydrophobicity increases the likelihood that the GDE will flood with electrolyte, which has a number of negative impacts on the performance for CO2 reduction. Firstly, the motivation for using GDEs is that CO2 solubility is low, so waiting for CO2 to dissolve and then diffuse towards the catalyst results in a slow rate of reduction. GDEs have mass transport in the gas phase, so that when CO2 dissolves in the electrolyte, it is already in close proximity to the catalyst, giving a much faster rate of reduction. A flooded GDE means that CO2 mass transport occurs mainly in the liquid phase, and so the rate of reduction is slow. Secondly, the flooded GDE brings the conductive carbon layer within the GDE into contact with the electrolyte. Carbon is active towards water reduction, and so the flooded GDE results in more of the applied charge being used for H2 evolution, lowering the .

The GDE flooding has been the focus of our investigations into the relatively poor stability of the electrodes for CO2 reduction, since it can be seen that the copper catalyst remains even when no further C2H4 is detected. Disassembling the apparatus to dry the flooded GDE results in the copper oxidising, resulting in a decreased performance once the GDE is reassembled. GDE flooding can be combatted by increasing the CO2 flow rate so that the backpressure will increase. However, increasing the flow of CO2 through the system decreases the residence time of CO2 at the catalyst, which will favour products with fewer electron transfers such as CO or CH4. The decreased residence time will also increase the proportion of unreacted CO2 in the outflow gas, making the process more wasteful. This could be mitigated by using a cyclic gas flow with a CO2 reservoir, but the Faradaic efficiency would remain low, making the process energetically wasteful.

When considering the next steps in the use of PIMs to enhance catalysts for CO2 reduction, the next advance will come from lessening the negative impact of the polymer on the hydrophobicity of the GDE whilst maintaining the favourable triphasic environment for the CO2 reduction. This change will not come from further manipulation of the PIMs loading, as the 0.01 mg cm-2 loading already provides a sizeable increase in  and decrease in the Tafel slope, whilst having a minimal impact on the starting hydrophobicity. Instead, work should focus on changing the nature of the polymer itself to increase the starting hydrophobicity, whilst maintaining the CO2 storage properties.

It is worth noting that, although the PIMs did reduce the starting hydrophobicity, all PIMs coated samples were substantially more resistant to changes in the surface hydrophobicity after periods of prolonged operation. The hydrated PIMs layer appears to have a slow rate of water transfer out of the PIMs and into the GDE itself. This is likely the reason that the 0.01 mg cm-2 coating outperformed the bare CO2 sample for stability during potentiostatic CO2 reduction, even though the starting hydrophobicity was slightly reduced. The field of triphasic polymers is growing, with a number of different PIMs (Marken et al., 2019), metal organic frameworks (González-Martínez et al., 2017), clays (Kadoura et al., 2016), zeolites (Ho et al., 2015) and porous carbons (Billemont et al., 2013) being potential candidates. This work acts as a proof on concept for the benefits of the triphasic environment for CO2 reduction. If the polymer layer can be manipulated to give an increase in the starting hydrophobicity, then this will provide a simple and effective means of enhancing both the activity and the stability of GDEs for CO2 reduction to C2H4. This could be simply applied to any of the presently leading engineered catalysts for selective CO2RR towards C2H4 to drive these materials towards the end goal of catalysts that can give high selectivity even at industrially relevant current densities.

# Conclusions

A 0.01 mg cm-2 PIMs layer effectively increased the activity, selectivity and stability of a copper GDE for targeted CO2 reduction to C2H4. The mechanism of this improvement is likely to be analogous to the reported improvements seen for oxygen reduction catalysts, where the porous polymer is able to store dissolved CO2 in a triphasic environment for facile reduction. The positive impact of PIMs on the catalyst properties must be compromised against the negative impact on the hydrophobicity of the electrode surface. Large PIMs loadings reduce the hydrophobicity to such an extent that water reduction out competes CO2 reduction, giving a lower C2H4 yield. However, the PIMs layers are also more stable to changes in surface hydrophobicity after prolonged operation, so a small loading was able to increase the overall stability of the GDE. So long as an appropriate compromise loading is chosen, PIMs offer a simple means to enhance the performance of leading copper GDEs for the electrochemical synthesis of C2H4 from CO2 reduction.

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# References

Billemont, P., Coasne, B., De Weireld, G., 2013. Adsorption of carbon dioxide, methane, and their mixtures in porous carbons: Effect of surface chemistry, water content, and pore disorder. Langmuir 29, 3328-3338.

Bui, M., Adjiman, C.S., Bardow, A., Anthony, E.J., Boston, A., Brown, S., Fennell, P.S., Fuss, S., Galindo, A., Hackett, L.A., Hallett, J.P., Herzog, H.J., Jackson, G., Kemper, J., Krevor, S., Maitland, G.C., Matuszewski, M., Metcalfe, I.S., Petit, C., Puxty, G., Reimer, J., Reiner, D.M., Rubin, E.S., Scott, S.A., Shah, N., Smit, B., Trusler, J.P.M., Webley, P., Wilcox, J., Mac Dowell, N., 2018. Carbon capture and storage (CCS): The way forward. Energy Environ. Sci. 11, 1062-1176.

Bushuyev, O.S., De Luna, P., Dinh, C.T., Tao, L., Saur, G., van de Lagemaat, J., Kelley, S.O., Sargent, E.H., 2018. What should we make with CO2 and how can we make it? Joule 2, 825-832.

Carta, M., Malpass-Evans, R., Croad, M., Rogan, Y., Jansen, J.C., Bernardo, P., Bazzarelli, F., McKeown, N.B., 2013. An efficient polymer molecular sieve for membrane gas separations. Science 339, 303-307.

Dinh, C.-T., Burdyny, T., Kibria, M.G., Seifitokaldani, A., Gabardo, C.M., García de Arquer, F.P., Kiani, A., Edwards, J.P., De Luna, P., Bushuyev, O.S., Zou, C., Quintero-Bermudez, R., Pang, Y., Sinton, D., Sargent, E.H., 2018. CO2 electroreduction to ethylene via hydroxide-mediated copper catalysis at an abrupt interface. Science 360, 783-787.

Endrődi, B., Kecsenovity, E., Samu, A., Darvas, F., Jones, R.V., Török, V., Danyi, A., Janáky, C., 2019. Multilayer electrolyzer stack converts carbon dioxide to gas products at high pressure with high efficiency. ACS Energy Lett. 4, 1770-1777.

Feaster, J.T., Shi, C., Cave, E.R., Hatsukade, T., Abram, D.N., Kuhl, K.P., Hahn, C., Nørskov, J.K., Jaramillo, T.F., 2017. Understanding selectivity for the electrochemical reduction of carbon dioxide to formic acid and carbon monoxide on metal electrodes. ACS Catal. 7, 4822-4827.

Feng, Y., Li, Z., Liu, H., Dong, C., Wang, J., Kulinich, S.A., Du, X., 2018. Laser-prepared CuZn alloy catalyst for selective electrochemical reduction of CO2 to ethylene. Langmuir 34, 13544-13549.

Gao, S., Lin, Y., Jiao, X., Sun, Y., Luo, Q., Zhang, W., Li, D., Yang, J., Xie, Y., 2016. Partially oxidized atomic cobalt layers for carbon dioxide electroreduction to liquid fuel. Nature 529, 68.

Gattrell, M., Gupta, N., Co, A., 2006. A review of the aqueous electrochemical reduction of CO2 to hydrocarbons at copper. J. Electroanal. Chem. 594, 1-19.

González-Martínez, G.A., Zárate, J.A., Martínez, A., Sánchez-González, E., Álvarez, J.R., Lima, E., González-Zamora, E., Ibarra, I.A., 2017. Confinement of alcohols to enhance CO2 capture in MIL-53(Al). RSC Adv. 7, 24833-24840.

Ho, L.N., Schuurman, Y., Farrusseng, D., Coasne, B., 2015. Solubility of gases in water confined in nanoporous materials: ZSM-5, MCM-41, and MIL-100. J. Phys. Chem. C 119, 21547-21554.

Hoang, T.T.H., Verma, S., Ma, S., Fister, T.T., Timoshenko, J., Frenkel, A.I., Kenis, P.J.A., Gewirth, A.A., 2018. Nanoporous copper–silver alloys by additive-controlled electrodeposition for the selective electroreduction of CO2 to ethylene and ethanol. J. Am. Chem. Soc. 140, 5791-5797.

Hori, Y., Takahashi, I., Koga, O., Hoshi, N., 2003. Electrochemical reduction of carbon dioxide at various series of copper single crystal electrodes. J. Mol. Catal. A: Chem. 199, 39-47.

Hussain, J., Jónsson, H., Skúlason, E., 2018. Calculations of product selectivity in electrochemical CO2 reduction. ACS Catal. 8, 5240-5249.

Jouny, M., Luc, W., Jiao, F., 2018. General techno-economic analysis of CO2 electrolysis systems. Ind. Eng. Chem. Res. 57, 2165-2177.

Kaczur, J.J., Yang, H., Liu, Z., Sajjad, S.D., Masel, R.I., 2018. Carbon dioxide and water electrolysis using new alkaline stable anion membranes. Front. Chem. 6, 263.

Kadoura, A., Narayanan Nair, A.K., Sun, S., 2016. Adsorption of carbon dioxide, methane, and their mixture by montmorillonite in the presence of water. Microporous Mesoporous Mater. 225, 331-341.

König, M., Vaes, J., Klemm, E., Pant, D., 2019. Solvents and supporting electrolytes in the electrocatalytic reduction of CO2. iScience 19, 135-160.

Kortlever, R., Shen, J., Schouten, K.J.P., Calle-Vallejo, F., Koper, M.T.M., 2015. Catalysts and reaction pathways for the electrochemical reduction of carbon dioxide. J. Phys. Chem. Lett. 6, 4073-4082.

Lin, S., Diercks, C.S., Zhang, Y.-B., Kornienko, N., Nichols, E.M., Zhao, Y., Paris, A.R., Kim, D., Yang, P., Yaghi, O.M., Chang, C.J., 2015. Covalent organic frameworks comprising cobalt porphyrins for catalytic CO2 reduction in water. Science 349, 1208-1213.

Liu, M., Pang, Y., Zhang, B., De Luna, P., Voznyy, O., Xu, J., Zheng, X., Dinh, C.T., Fan, F., Cao, C., de Arquer, F.P.G., Safaei, T.S., Mepham, A., Klinkova, A., Kumacheva, E., Filleter, T., Sinton, D., Kelley, S.O., Sargent, E.H., 2016. Enhanced electrocatalytic CO2 reduction via field-induced reagent concentration. Nature 537, 382.

Liu, X., Xiao, J., Peng, H., Hong, X., Chan, K., Nørskov, J.K., 2017. Understanding trends in electrochemical carbon dioxide reduction rates. Nat. Commun. 8, 15438.

Lum, Y., Ager, J.W., 2019. Evidence for product-specific active sites on oxide-derived Cu catalysts for electrochemical CO2 reduction. Nat. Catal. 2, 86-93.

Madrid, E., Lowe, J.P., Msayib, K.J., McKeown, N.B., Song, Q., Attard, G.A., Düren, T., Marken, F., 2019. Triphasic nature of polymers of intrinsic microporosity induces storage and catalysis effects in hydrogen and oxygen reactivity at electrode surfaces. ChemElectroChem 6, 252-259.

Marken, F., Madrid, E., Zhao, Y., Carta, M., McKeown, N.B., 2019. Polymers of intrinsic microporosity in triphasic electrochemistry: Perspectives. ChemElectroChem 6, 1-12.

Medina-Ramos, J., Pupillo, R.C., Keane, T.P., DiMeglio, J.L., Rosenthal, J., 2015. Efficient conversion of CO2 to CO using tin and other inexpensive and easily prepared post-transition metal catalysts. J. Am. Chem. Soc. 137, 5021-5027.

Na, J., Seo, B., Kim, J., Lee, C.W., Lee, H., Hwang, Y.J., Min, B.K., Lee, D.K., Oh, H.-S., Lee, U., 2019. General technoeconomic analysis for electrochemical coproduction coupling carbon dioxide reduction with organic oxidation. Nat. Commun. 10, 5193.

Nam, D.-H., Bushuyev, O.S., Li, J., De Luna, P., Seifitokaldani, A., Dinh, C.-T., García de Arquer, F.P., Wang, Y., Liang, Z., Proppe, A.H., Tan, C.S., Todorović, P., Shekhah, O., Gabardo, C.M., Jo, J.W., Choi, J., Choi, M.-J., Baek, S.-W., Kim, J., Sinton, D., Kelley, S.O., Eddaoudi, M., Sargent, E.H., 2018. Metal–organic frameworks mediate Cu coordination for selective CO2 electroreduction. J. Am. Chem. Soc. 140, 11378-11386.

Ogura, K., 2013. Electrochemical reduction of carbon dioxide to ethylene: Mechanistic approach. J. CO2 Util. 1, 43-49.

Ogura, K., Ferrell, J.R., Cugini, A.V., Smotkin, E.S., Salazar-Villalpando, M.D., 2010. CO2 attraction by specifically adsorbed anions and subsequent accelerated electrochemical reduction. Electrochim. Acta 56, 381-386.

Ogura, K., Oohara, R., Kudo, Y., 2005. Reduction of CO2 to ethylene at three-phase interface effects of electrode substrate and catalytic coating. J. Electrochem. Soc. 152, D213-D219.

Ooka, H., Figueiredo, M.C., Koper, M.T.M., 2017. Competition between hydrogen evolution and carbon dioxide reduction on copper electrodes in mildly acidic media. Langmuir 33, 9307-9313.

Pletcher, D., 2015. The cathodic reduction of carbon dioxide—what can it realistically achieve? A mini review. Electrochem. Commun. 61, 97-101.

Rasul, S., Anjum, D.H., Jedidi, A., Minenkov, Y., Cavallo, L., Takanabe, K., 2015. A highly selective copper–indium bimetallic electrocatalyst for the electrochemical reduction of aqueous CO2 to CO. Angew. Chem. Int. Ed. 54, 2146-2150.

Romero Cuellar, N.S., Wiesner-Fleischer, K., Fleischer, M., Rucki, A., Hinrichsen, O., 2019. Advantages of CO over CO2 as reactant for electrochemical reduction to ethylene, ethanol and n-propanol on gas diffusion electrodes at high current densities. Electrochim. Acta 307, 164-175.

Rosen, J., Hutchings, G.S., Lu, Q., Forest, R.V., Moore, A., Jiao, F., 2015. Electrodeposited Zn dendrites with enhanced CO selectivity for electrocatalytic CO2 reduction. ACS Catal. 5, 4586-4591.

Sánchez, O.G., Birdja, Y.Y., Bulut, M., Vaes, J., Breugelmans, T., Pant, D., 2019. Recent advances in industrial CO2 electroreduction. Current Opinion in Green and Sustainable Chemistry 16, 47-56.

Schouten, K.J.P., Qin, Z., Pérez Gallent, E., Koper, M.T.M., 2012. Two pathways for the formation of ethylene in CO reduction on single-crystal copper electrodes. J. Am. Chem. Soc. 134, 9864-9867.

Takahashi, I., Koga, O., Hoshi, N., Hori, Y., 2002. Electrochemical reduction of CO2 at copper single crystal Cu(s)-[n(111)×(111)] and Cu(s)-[n(110)×(100)] electrodes. J. Electroanal. Chem. 533, 135-143.

Tang, W., Peterson, A.A., Varela, A.S., Jovanov, Z.P., Bech, L., Durand, W.J., Dahl, S., Nørskov, J.K., Chorkendorff, I., 2012. The importance of surface morphology in controlling the selectivity of polycrystalline copper for CO2 electroreduction. Phys. Chem. Chem. Phys. 14, 76-81.

Varela, A.S., Kroschel, M., Reier, T., Strasser, P., 2016. Controlling the selectivity of CO2 electroreduction on copper: The effect of the electrolyte concentration and the importance of the local pH. Catal. Today 260, 8-13.

Varela, A.S., Sahraie, N.R., Steinberg, J., Ju, W., Oh, H.S., Strasser, P., 2015. Metal‐doped nitrogenated carbon as an efficient catalyst for direct CO2 electroreduction to CO and hydrocarbons. Angew. Chem. Int. Ed. 54, 10758-10762.

Vasileff, A., Xu, C., Jiao, Y., Zheng, Y., Qiao, S.-Z., 2018. Surface and interface engineering in copper-based bimetallic materials for selective CO2 electroreduction. Chem 4, 1809-1831.

Verdaguer-Casadevall, A., Li, C.W., Johansson, T.P., Scott, S.B., McKeown, J.T., Kumar, M., Stephens, I.E.L., Kanan, M.W., Chorkendorff, I., 2015. Probing the active surface sites for CO reduction on oxide-derived copper electrocatalysts. J. Am. Chem. Soc. 137, 9808-9811.

Wakerley, D., Lamaison, S., Ozanam, F., Menguy, N., Mercier, D., Marcus, P., Fontecave, M., Mougel, V., 2019. Bio-inspired hydrophobicity promotes CO2 reduction on a Cu surface. Nat. Mater. 18, 1222-1227.

Wang, Y., Shen, H., Livi, K.J.T., Raciti, D., Zong, H., Gregg, J., Onadeko, M., Wan, Y., Watson, A., Wang, C., 2019. Copper nanocubes for CO2 reduction in gas diffusion electrodes. Nano Lett. 19, 8461-8468.

Yano, H., Shirai, F., Nakayama, M., Ogura, K., 2002. Efficient electrochemical conversion of CO2 to CO, C2H4 and CH4 at a three-phase interface on a Cu net electrode in acidic solution. J. Electroanal. Chem. 519, 93-100.

Yano, H., Tanaka, T., Nakayama, M., Ogura, K., 2004. Selective electrochemical reduction of CO2 to ethylene at a three-phase interface on copper(I) halide-confined Cu-mesh electrodes in acidic solutions of potassium halides. J. Electroanal. Chem. 565, 287-293.

Yano, J., Morita, T., Shimano, K., Nagami, Y., Yamasaki, S., 2007. Selective ethylene formation by pulse-mode electrochemical reduction of carbon dioxide using copper and copper-oxide electrodes. J. Solid State Electrochem. 11, 554-557.

Zhang, J., Luo, W., Züttel, A., 2019. Self-supported copper-based gas diffusion electrodes for CO2 electrochemical reduction. J. Mater. Chem. A 7, 26285-26292.