Author:
Hedditch, Connie R

Title:
3D-printable conjugated microporous polymer electrodes for carbon capture and conversion

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3D-Printable Conjugated Microporous Polymer Electrodes for Carbon Capture and Conversion

By

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A dissertation submitted to the University of Bristol in accordance with the requirements of the degree of MASTERS BY RESEARCH in the Faculty of Science.

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Abstract

In this study, polytriphenylamine was used as a cathode for electrochemical CO$_2$ reduction to yield formate and methanol at moderate overpotentials and Faradaic efficiencies. Suitable polymer support networks were identified and blending techniques were established to formulate composite polymeric electrodes which could be processed by 3D printing.

Polyethylene oxide and polypropylene support networks were used in the first part of the study, and the information obtained using these materials informed the choice of PIM-1, a polymer of intrinsic microporosity, as the final support network investigated. Product actualisation was achieved using the polypropylene composites, as an electrode with complex architecture was printed successfully.

The PIM-1-based composites showed the highest activity towards electrochemical CO$_2$ reduction of the composites investigated, owing to the affinity of PIM-1 to CO$_2$ and its intrinsic microporosity. CO$_2$ was selectively reduced to methanol at a low overpotential of -0.5 V vs RHE with a Faradaic efficiency of 91.2%. This study shows that mechanically-robust electrodes for CO$_2$ reduction containing conjugated microporous polymers can be formulated and their geometry precisely controlled by 3D printing. Printable and porous polymer materials show promise as electrode materials for ECO$_2$R.
COVID-19 Impact Statement

The University of Bristol School of Chemistry had to implement strict government guidelines, owing to the COVID-19 global pandemic. These guidelines outlined rules of social distancing and self-isolation for those who were in contact/infected with COVID-19. This had a huge impact on research-based activities, not only within the UK, but globally.

Due to the number of researchers within the Faul Research Group and the space within the offices which did not permit adequate social distancing, the research group was forced to operate with a 50% capacity. This meant for the first 10 months of my study, I only had access to the laboratory for 1 week out of every 2 weeks spent conducting my MRes.

Social distancing rules not only affected the time I was able to spend in the laboratory; access to/training for specialised equipment was limited; there were often long delays on chemical orders; I did not have the usual opportunities for socialising as a new student in a new city; people with expertise in my field of research such as PhD students and postdocs were more to difficult to contact and were also struggling with the impact that the COVID-19 pandemic had on their research.

My supervisor, Prof Charl F. J. Faul, did an excellent job of making himself available during these difficult times for project updates, problem-solving and general chats, for which I am very thankful. He also made sure that through online socials and regular online group meetings, I was able to meet other members of the research group, hear about their research and present the work that I have been doing to get invaluable feedback. However, I think that Charl can agree that meetings and conferences over Zoom do not provide the same experience and learning outputs that face-to-face meetings have, and communicating problems that you are facing is made more difficult.

COVID-19 had a huge impact on my studies and sometimes I feel frustrated about how difficult it made research at times had it not spread to the extent that we were forced to face. I also often wonder what different directions I could have taken my research and how much more I could have done.

However, I do know that I am very tired of Zoom meetings.
Acknowledgments

I would firstly like to express my sincere thanks to my supervisor Professor Charl F. J. Faul for the invaluable support and advice he gave me throughout the year and the generosity with which he gave me his time. I am extremely grateful for the way he welcomed me into his research group and feel lucky to have had him as my supervisor.

I would also like to express my gratitude to the Faul Research Group, especially Dr Ben Baker for his continuous support and guidance throughout my MRes; Dr Veronica Del Angel Hernandez for providing me with a good foundation with which to start my research and her input with my learning of electrochemistry; Marcos Villeda Hernandez and Sam Deeks for their help with 3D printing and help with problem-solving; Julia Maxwell for doing her project alongside me, her friendship and constant encouragement. I am also thankful to the staff at the University of Bristol who worked in the background so that I could go into campus during the lockdown and use the facilities to help complete my project.

I would like to thank my boyfriend Robbie, housemates Joe, James and Mike, and friend Antonia for their support and the laughs that we had whilst I was navigating new jobs and the completion of my MRes. Finally, and most importantly, I would like to thank my parents. Their endless support and belief in me has been a constant source of motivation throughout the last two years, which I would not have been able to complete without them.
Author’s Declaration

I declare that the work in this dissertation was carried out in accordance with the requirements of the University’s Regulations and Code of Practice for Research Degree Programmes and that it has not been submitted for any other academic award. Except where indicated by specific reference in the text, the work is the candidate’s own work. Work done in collaboration with, or with the assistance of, others, is indicated as such. Any views expressed in the dissertation are those of the author. SIGNED: ........................................ DATE: 14/11/2022
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Introduction

Anthropogenic greenhouse gas (GHG) emissions have warmed the planet by 1.09°C since the pre-industrial era.\textsuperscript{1} Carbon dioxide (CO\textsubscript{2}) is one of the main GHGs contributing to climate change,\textsuperscript{1} so its capture and use as a one-carbon (C1) building block in chemical manufacture has received ever-increasing attention from the scientific community.\textsuperscript{2} This approach is attractive owing to the sustainability of the concept and the potential to expand the low-carbon economy.

Electrochemical CO\textsubscript{2} reduction (ECO\textsubscript{2}R) uses CO\textsubscript{2} as a C1 building block, producing more reduced chemical species through the input of electrical energy. Since its discovery in 1985,\textsuperscript{3} there has been a huge effort to understand the process and develop materials for its commercialisation. With tunable functionality and porosity, a permanently microporous skeleton, π-conjugation and excellent thermal and chemical stability, conjugated microporous polymers (CMPs) present a low-cost material choice for this application. Their use thus far has been limited due to their poor processability, arising from their highly cross-linked 3D structure.\textsuperscript{4–7}

1.1 CO\textsubscript{2} Capture, Storage and Utilisation

1.1.1 Motivation for CO\textsubscript{2} Capture, Storage and Utilisation

GHGs, such as carbon and nitrous oxides, methane and fluorocarbons are responsible for the increase in global temperature as a result of the greenhouse effect. These gases have historically maintained Earth’s temperature meaning they are essential to life; the strong absorption they show for the sun’s infrared energy warms the Earth’s surface upon re-emission.\textsuperscript{8} However, since the pre-industrial era, unprecedented human activity has increased GHG concentrations to record levels.\textsuperscript{1,9}

At a global temperature of +1.09°C since the pre-industrial era,\textsuperscript{10} the Earth has seen adverse weather events,\textsuperscript{10,11} wildfires,\textsuperscript{10} rising sea levels,\textsuperscript{12–14} and a huge loss of wildlife.\textsuperscript{15,16} Climate change is impacting the natural world and simultaneously introducing a wealth of socioeconomic effects to humanity, where developing countries and marginalised com-
Communities are disproportionately affected. In 2015, the Paris Agreement set out a global framework to avoid catastrophic climate change by limiting global warming to below 2°C, and aim for a 1.5°C maximum. The 2021 COP26 summit saw countries agree to keep the 1.5°C target alive, but even in the most optimistic scenario with the global implementation of all net-zero targets, long-term targets and national determined contributions, a global temperature increase of 1.8°C is estimated, exceeding the maximum which was agreed upon.

In order to meet- or even excel- the targets defined in COP26, carbon capture, utilisation and storage (CCUS) technology must be developed to remove excess GHGs from the atmosphere whilst the global dependence on fossil fuels shifts towards renewable and low-carbon energy. Of the GHGs to remove, CO₂ is one of the most important since it is responsible for the largest proportion of human-driven global warming.

1.1.2 Types of CCUS

This section will discuss the various types of CCUS and is split into two sections: carbon capture processes, and then carbon capture and storage or carbon capture and utilisation.

Carbon Capture

Industrial sources of CO₂, such as those from power plants, iron and steel production and oil refineries, are suitable for point-source carbon capture. There are 3 types of point-source capture: pre-combustion capture, post-combustion capture and oxyfuel combustion.

Pre-combustion capture involves capturing CO₂ as an undesirable product of an intermediate reaction. Post-combustion capture separates CO₂ from waste gas streams following the industrial process. Oxy-fuel combustion can only be used in processes which involve combustion, such as fossil-fuel power plants. Fuel is burned with pure oxygen, allowing for complete combustion, producing flue gas with high CO₂ concentrations which avoids the need for selective carbon capture. However, this process requires a pure oxygen source which itself has a high carbon footprint due to difficulty in its production.

Point-source capture is not perfect, and often, not all CO₂ produced by industrial processes is captured. Old plants cannot be retrofitted with capture technology, and the
determines the diversity of processes emitting CO₂ makes one-size-fits-all capture technology unsuitable. Furthermore, other sectors with high CO₂ emissions, such as transport, are unsuitable for this type of capture but must still be accounted for in terms of climate change mitigation. Here, capturing CO₂ directly from the atmosphere is a suitable approach.

Direct air capture (DAC) plants extract CO₂ from the atmosphere by using solid or liquid sorbents which strongly bind to the GHG. There are 2 types of DAC: high-temperature (HT) aqueous solution DAC and low-temperature (LT) solid sorbent DAC, in which both types of adsorbents are brought into contact with ambient air and CO₂ is captured to form carbonates (HT aqueous solution) or pure CO₂ gas streams (LT solid sorbent). The plants themselves require a lot of energy to operate, utilising large fans to maintain a constant air flow over the solid and liquid sorbents, and high temperatures or vacuums to liberate the captured CO₂.

Carbon capture technology has been commercialised- there are 21 large-scale capture projects globally as of 2020- yet its deployments has been slow, with the additional cost of carbon capture to industrial processes regularly hailed as the rate-limiting factor. The sources of CO₂ also influence the cost of capture, highlighted in Figure 1.1.

![Figure 1.1: Cost of carbon capture by plant type.](image)

DAC plants are currently the most expensive approach, with costs ranging from $134-342/tonne of CO₂ captured. More cost-effective capture materials may provide the drop...
in price that is needed for the surge in operating carbon capture plants.

**Storage and Utilisation**

With the CO₂ captured, focus shifts to where the GHG can be stored (carbon capture and storage) or how to use it (carbon capture and utilisation).

Once captured, CO₂ is pressurised to form supercritical CO₂ and then shipped or transported via pipelines to be stored in the ground, ocean or as mineral carbonates. Owing to the knowledge and experience in the oil and gas industry, the first option, in which CO₂ is injected into depleted oil and gas reservoirs or deep saline aquifers, is the most promising. There are few practical examples of storing CO₂ in the ocean bed despite the capacity at which it can be stored at. The main concerns here are possible leaks, and the damage concentrated streams of CO₂ may cause to the environment.

Carbon capture and storage (CCS) is faced with the disadvantage that it requires large capital investment with no return, and may simply not be viable in some countries due to limited geological storage capacity. Therefore, utilising the captured CO₂ to produce value-added products is a more attractive approach, incentivising the process by generating economic return.

There are many examples of this including mineral carbonation for building materials, enhanced oil and coal-bed methane recovery (however this retains the global dependence on fossil fuels), industrial chemical synthesis and biofuel production from algae.

Finally, electrochemical CO₂ reduction (ECO₂R) is another process utilising CO₂ as a building-block to obtain a wide variety of value-added products. Using electrical energy, a catalyst and water, CO₂ can be reduced to liquid fuels, syngas components and useful synthetic chemicals. The liquid fuels can be incorporated into existing internal combustion engines and the aviation industry, decarbonising the transportation sector. Furthermore, when these hydrocarbons and liquid fuels are produced through the input of renewable energy, ECO₂R can be considered as a form of long-term energy storage.
For capture and utilisation processes such as DAC and ECO$_2$R which consume energy, it is important that the energy comes from renewable sources to maximise the potential of the CCUS technologies to close the carbon cycle. As the cost of renewable energy becomes competitive with that of oil and gas, CO$_2$ breakeven costs, which “represent the incentive per tonne of CO$_2$ utilised that would be necessary to make the utilisation pathway economic” will become lower, increasing the motivation to adopt this type of technology.

Costs can also be reduced through the ongoing research into materials used for capture, storage and utilisation. CO$_2$ capture is the most costly part of CCS and CCU. The next subsection will introduce the challenges of carbon capture, materials used for this application and their requirements.

### 1.1.3 CO$_2$ Capture Chemistry and Requirements

CO$_2$ is an inert, chemically-stable molecule and may be captured by a variety of capture sorbents. Capture sorbents are materials which allow for sorption of molecules, either by physical or chemical absorption or adsorption. Figure 1.3 shows sorption pathways for a number of materials which may be used for point-source capture.
The sorbent must be selective for CO$_2$ over other components in a gas stream (for point-source capture) or the atmosphere (for DAC). Sorbents can be designed according to experimental and computational research which evaluates functional groups and heteroatoms that interact strongly with CO$_2$. Nitrogen-containing or amine-functionalised materials have good performance because of favourable interactions between CO$_2$ and nitrogen moieties.

One of the most industrially mature CO$_2$ separation and capture sorbents is monoethanol amine (MEA). This is a liquid absorbent which reacts with CO$_2$ in gas streams in a process called amine wet scrubbing to form a carbamate. The carbamate is subsequently heated to regenerate the sorbent and gas. The regeneration step can cause covalent bond breakage, followed by amine loss, so MEA loses efficacy over time.

The energy requirements of the regeneration step are costly, and material stability is clearly an issue. To reduce costs, solid porous materials are emerging as more economical CO$_2$ separation and capture materials. They exhibit greater durability over many cycles and require low regeneration energies because they adsorb CO$_2$ rather than absorb (Section 1.2.1 will discuss the chemistry of adsorption in more detail). They can be used at a range of CO$_2$ partial pressures for capture, and their functionality is tunable to the target gas, meaning the introduction of certain functional groups and heteroatoms increases CO$_2$ capture concentrations.

For example the quadrupole moment of CO$_2$ allows for strong dipole-quadrupole interactions between the CO$_2$ C atoms and N atoms in amine groups. Hydrogen bonding
also occurs between the electronegative oxygen atoms and electropositive hydrogen atoms in NH\textsubscript{2}-containing groups, increasing the likelihood of intramolecular interactions.\textsuperscript{41–43} N-basic sites also act as an electron-donor in Lewis acid-base interactions, where the electropositive C on the CO\textsubscript{2} molecule accepts the lone pair.\textsuperscript{44–46} It is clear that the inclusion of N moieties in promising carbon capture materials improves adsorption capabilities.\textsuperscript{7,46–48}

Some aromatic compounds can bind with CO\textsubscript{2} by \(\pi-\pi\) interactions\textsuperscript{35} and electrostatic in-plane interactions\textsuperscript{34} Due to the resonance effect these molecules exhibit, they show enhanced stability for CO\textsubscript{2} interactions.\textsuperscript{34} N-containing aromatic compounds show stronger interaction with CO\textsubscript{2} through Lewis acid/base interactions than pi-pi stacking\textsuperscript{35} but enhancing the aromaticity of a material undoubtedly strengthens interactions between CO\textsubscript{2} and the material.\textsuperscript{35} Figure 1.4 depicts some of the interaction mechanisms discussed.

![Figure 1.4: CO\textsubscript{2} interaction with amine groups and benzene rings.](image)

| Table 1.1 highlights important parameters that a solid sorbent must satisfy before it can be considered for CO\textsubscript{2} capture in industry. This includes the selectivity over other gases (to obtain a near-pure 99\% CO\textsubscript{2} gas stream, the sorbent must be at least 100 times more selective for CO\textsubscript{2} over other gases in the feed) and the kinetics, or speed, of CO\textsubscript{2} uptake.\textsuperscript{32} | }
Table 1.1: Industrial benchmarks for CO₂ capture.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Industrial Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity</td>
<td>2 mmol CO₂ per g of sorbent</td>
</tr>
<tr>
<td>Recyclability</td>
<td>1000 cycles</td>
</tr>
<tr>
<td>Selectivity</td>
<td>100 (CO₂/other gases in gas stream)</td>
</tr>
<tr>
<td>Stability</td>
<td>Withstand 150°C temperatures and boiling water, HCl, SOₓ. Have good mechanical strength.</td>
</tr>
<tr>
<td>Cost</td>
<td>50$</td>
</tr>
<tr>
<td>Kinetics</td>
<td>1 mmolg⁻¹min⁻¹</td>
</tr>
</tbody>
</table>

Owing to the traction solid sorbents are receiving in research, they may soon outperform the current state-of-the-art chemical absorbents; solid sorbents offer many advantages, such as ease of regeneration. The next section will introduce adsorption chemistry and porous materials and the applications for which they can be used.

1.2 Porous Materials

1.2.1 Classification and Adsorption Chemistry

Porous materials are materials which contain pores or voids and generally have high surface areas per gram of material. They are classified based on their pore sizes as shown in Table 1.2.

Table 1.2: Pore sizes and corresponding classification.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Pore Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microporous</td>
<td>&lt; 2 nm</td>
</tr>
<tr>
<td>Mesoporous</td>
<td>2 - 50 nm</td>
</tr>
<tr>
<td>Macroporous</td>
<td>&gt; 50 nm</td>
</tr>
</tbody>
</table>

Porous solids capture gas via adsorption. Adsorption is the enrichment of one or more components in an interfacial layer (its counterpart, desorption, defines the opposite process), and is different to the process of absorption, in which molecules penetrate the surface layer and enter the structure of the bulk solid. It is difficult to distinguish between adsorption and absorption, so sorption is a convenient term to describe the wider process.
Adsorption may occur by either chemisorption or physisorption. Chemisorption involves the formation of chemical bonds between gas molecules (adsorptive) and a solid surface (adsorbent), resulting in an activation energy. Due to the specificity of the interaction, the location at which chemisorption occurs is limited to the regions on the adsorbent containing molecules that the adsorptive may form chemical bonds with. This means that chemisorption is restricted to a single layer of chemically-bound molecules.

Physisorption is a phenomena in which an adsorptive is brought into contact with the surface of an adsorbent. The intermolecular forces involved in this process are those responsible for the condensation of vapours and the tendency of real gases to deviate from ideal gas-laws.

Physisorption is accompanied with low heats of adsorption without any structural changes occurring to the adsorbent’s surface. Equilibrium is reached quickly since no activation energy is required for capture of the adsorptive. Physisorption is fully reversible and may lead to adsorption to greater than one layer of adsorptive, unlike chemisorption. Physisorbed molecules are not restricted to specific sites and are free to cover the entire solid surface to which they are adsorbed. Because of this, the surface area may be calculated rather than the number of interaction sites as would be the case for chemisorption.

Physisorption, or adsorption, isotherms must be obtained to accurately determine the surface area of a solid material. There are different procedures to do this, but in this study, the determination of adsorption isotherms was achieved using an Autosorb iQ gas adsorption analyser, which uses the static volumetric method.

In this method, the adsorbent is treated to remove any physisorbed molecules in a drying and degassing step. Once complete, the void volume in the sample cell of known volume is measured using helium gas at room temperature and the measurement temperature. A known quantity of pure gas, usually nitrogen (N₂), is then admitted. The pressure in the cell is allowed to reach equilibrium and is then measured. The amount of gas adsorbed is the difference between the amount of gas admitted and the quantity of gas filling the void volume. From this process, the volume of gas adsorbed is plotted against the partial pressure of the gas, yielding adsorption isotherms.

Pore size influences the strength of adsorbent-adsorbate and adsorbate-adsorbate interactions and therefore the amount of gas adsorbed. The adsorption potential varies as a
function of distance from the adsorbent surface. The graphs in Figure 1.5 illustrate this by plotting the adsorption potential, $\epsilon$, as a function of the adsorptive distance from the adsorbate surface for different pore sizes.

(a) Macroporous solids.  
(b) Mesoporous solids.  
(c) Microporous solids.

Figure 1.5: Adsorption potential for different pore sizes, adapted from S. Lowell.

Macropores, Figure 1.5a, are so large they can be considered as planar surfaces. The process of micropore filling is dominated almost entirely by the interactions between fluid molecules and the pore walls due to complete overlapping of adsorption potentials as seen in Figure 1.5c. However in mesopores, the adsorption behaviour is also influenced by the attractive interactions between fluid molecules. This results in pore condensation in which gas condenses to a liquid-like phase in pores at a pressure less than the saturation pressure $P_0$ of the bulk fluid.

This information can be used to classify adsorption isotherms based on pore size. There are 6 IUPAC-defined isotherms, as shown in Figure 1.6. Many adsorbents exhibit a range of pore sizes, such as a combination of micro- and mesopores so it is not uncommon for adsorption isotherms to have features of different isotherm types.

The type I isotherm is known as the reversible isotherm, and is obtained when adsorption is limited to a few molecular layers. This is encountered in chemisorption, but is also indicative of a microporous material; micropore filling occurs at low partial pressures resulting from narrow pore with and high adsorption potentials. Adsorption reaches a limiting value as $P/P_0 \rightarrow 1$ because available adsorption sites have already been filled.
Type II isotherms are typically obtained for non-porous or macroporous adsorbents, where multilayer adsorption may occur freely. The inflection point marked as “B” in Figure 1.6 indicates the point at which monolayer adsorption is completed and multilayer adsorption begins.

Type III isotherms indicate that adsorbate-adsorbent interactions are weak, since a high partial pressure is required to encourage adsorption. Type IV isotherms are typical for mesoporous materials due to the hysteresis loop, associated with pore condensation. The plateau of adsorbed gas at higher partial pressures indicates complete pore filling and the inflection at low partial pressures is attributed to the transition from monolayer to multilayer adsorption.

Type V isotherms show pore condensation and hysteresis but for weak interactions between the adsorbate and the adsorbent. Type VI isotherms demonstrate stepwise multilayer adsorption on a uniform, non-porous surface.

The measurement of gas uptake by adsorption remains to be the most popular way to measure the surface area of porous solids. The Brunauer-Emmett-Teller (BET)
method is the theory most widely applied for the determination of the surface area of solid materials. The next subsection will introduce the mode of measurement and the basis of the theory.

1.2.2 BET Theory

The BET theory extends the Langmuir theory of gas adsorption (which assumes adsorption is limited to a monolayer) to multilayer adsorption.\textsuperscript{31} The application of the BET equation, (Equation 1.1\textsuperscript{49,50}) is used to determine the surface area of solid materials.

\begin{equation}
\frac{1}{n \left( \frac{P_0}{P} - 1 \right)} = \frac{1}{n_mC} + \frac{C - 1}{n_mC} \left( \frac{P}{P_0} \right)
\end{equation}

\(n\) is the amount of gas adsorbed at the relative pressure \(P/P_0\), \(n_m\) is the specific monolayer capacity of the adsorbate. \(C\) is related to the energy of adsorption and, as explained above, is a value which gives an indication of the isotherm type.

**Total Surface Area Determination**

Equation 1.1 is a linear equation and can be manipulated such that \(n_m\) may be obtained. Plotting \((n(P/P_0-1))^{-1}\) against \(P/P_0\) in the range of \(0.05 \leq P/P_0 \leq 0.30\)\textsuperscript{49} gives the gradient (\(s\)) and the intercept (\(i\)) of Equation 1.1 as follows.

\begin{equation}
s = \frac{1}{n_mC}
\end{equation}

\begin{equation}
i = \frac{C - 1}{n_mC}
\end{equation}

Equations 1.2 and 1.3 can be manipulated to obtain \(n_m\).

\begin{equation}
n_m = \frac{1}{i + s}
\end{equation}

The molecular cross-sectional area, \(a_m\), occupied by the adsorbate molecule must be known to calculate the surface area. For \(N_2\), this is 0.162 nm\(^2\) at 77K.\textsuperscript{43} This value, along with \(n_m\) and Avogadro’s constant \(N\), is used to calculate the total surface area of the material, \(A_s\).
\[ A_s = n_m \cdot N \cdot a_m \] (1.5)

**Total Pore Volume Determination**

The total pore volume, \( V_p \), is derived from the amount of gas adsorbed at \( P/P_0 \approx 1 \) with the assumption that the pores are filled with condensed adsorptive in its liquid state. The total pore volume, \( V_{liq} \) is well defined for microporous and mesoporous materials, since the isotherm remains nearly horizontal for \( P/P_0 \rightarrow 1 \) \(^{49,51} \) (in the presence of macropores, the amount adsorbed as \( P/P_0 \) reaches unity is not well-defined, so pore volume for macroporous materials should not be evaluated from its physisorption isotherm). The limiting adsorption capacity can be identified assuming the temperature was carefully controlled\(^{52} \) \(^{51} \). The volume of nitrogen adsorbed, \( V_{ads} \), can be converted to the volume of liquid nitrogen \( V_{liq} \), and therefore the total pore volume, using equation \( 1.6 \):

\[ V_{liq} = \frac{P_a \cdot V_{ads} \cdot V_m}{R \cdot T} \] (1.6)

\( P_a \) and \( T \) are ambient pressure and temperature respectively and \( V_m \) is the molar volume of the liquid adsorbate. For \( N_2 \), this value is 34.7 cm\(^3\)/mol. The pores which do not fill below a relative pressure of 1 contribute negligibly to the overall surface area and pore volume.\(^{51} \) Because of this, the average pore size can be estimated from pore volume assuming a certain pore geometry. Equation \( 1.7 \) assumes a cylindrical pore geometry, giving the average pore radius, \( r_p \):\(^{53} \)

\[ r_p = \frac{2 \cdot V_{liq}}{A_s} \] (1.7)

**Non-Local Density Functional Theory and Monte Carlo Simulations**

Non-Local Density Functional Theory (NLDFT) and Grand Conical Monte Carlo simulations (GCMC) are the most advanced and widely applied processes for micro- and mesoporous pore analysis. For very narrow micropores, the Monte Carlo simulation is the most appropriate, so for this work, NLDFT is applied in the determination of pore size and pore size distribution (PSD).\(^{54} \)
For both techniques, a set of isotherms are calculated for a set of pore sizes for a given adsorptive. These isotherms are known as theoretical isotherms and they comprise the model database. The calculation of the PSD is based on a solution of the Generalised Adsorption Isotherm equation (GAI) which correlates the sets of theoretical adsorption/desorption isotherms with the experimental sorption isotherm \( N(P/P_0) \).

\[
N \left( \frac{P}{P_0} \right) = \int_{W_{MIN}}^{W_{MAX}} N \left( \frac{P}{P_0}, W \right) f(W) \, dW \tag{1.8}
\]

\( W \) is the pore width and \( N(P/P_0, W) \) is the isotherm on a single pore of width \( W \). \( f(W) \) is the pore size distribution. The pore size distribution is derived by solving the Equation 1.8 numerically. 

1.2.3 Types of Porous Materials and their Applications

Porous materials may be used for a wide variety of applications such as fluorescence sensing, photovoltaics, water purification, energy storage and drug delivery. As aforementioned, there are also many promising porous materials for CO\(_2\) capture such as activated carbons, zeolites and mesoporous silicas which are perhaps of the most industrially mature CO\(_2\) capture sorbents. However, poor stability and CO\(_2\) selectivities has precluded these materials from being used on an industrial scale.

In the past 30 years, research into porous materials has seen an exciting increase in the number of publications. Research has led to the discovery of new materials with unprecedented surface areas and functional-tunability, which present as promising candidates for the application of CO\(_2\) separation and capture.

Metal Organic Frameworks

Metal organic frameworks are organic-inorganic hybrid crystalline porous materials. They consist of a regular array of positively charged metal ions or metal ion clusters coordinated to organic linker molecules to form one-, two- or three-dimensional crystalline structures (as seen in Figure 1.7) which exhibit extremely high porosity. To date, MOFs hold the record for some of the highest surface areas seen in porous materials, with MOF DUT-60 holding the record with a surface area of 7839 m\(^2\)/g for porous crystalline solids.
MOFs may be used for a range of applications, such as gas adsorption, fluorescence sensing, medical applications and energy storage devices. Their multi-application abilities is due to the unprecedented chemical and structural tunability, in which their structure may be decorated with both organic and inorganic moieties. They are promising materials for CO$_2$ capture. However, in the presence of moisture, CO$_2$ selectivity diminishes since water outcompetes CO$_2$ in coordinating exposed metal sites.

Poor chemical, physical and thermal stability has prevented the advancement of these materials into industry. The stability of the materials depend on a number of factors, such as the metal-ligand coordination bond strength, linker rigidity, coordination number, surface hydrophobicity and framework interpenetration. Post-synthetic techniques, hydrophobic surface treatments and computational methods for the careful selection of the metal centres are being developed to improve MOF stability, but further work is required to industrialise these materials.

**Porous Organic Polymers**

Porous organic polymers (POPs) are a class of porous materials which are built via strong covalent linkages between various organic building blocks. They are further classified depending on their morphology. Crystalline POPs are represented by covalent organic frameworks (COFs) whereas amorphous POPs include hyper-crosslinked polymers (HCPs), polymers of intrinsic microporosity (PIMs), porous aromatic frameworks (PAFs) and conjugated microporous polymers (CMPs). These materials have huge application potentials owing to their tunable pore structure and size, specific surface area and functionality. Many POPs were only discovered approximately a decade ago, but owing to their design flexibility, have already gained huge research momentum.
COFs are two- or three-dimensional structures that are obtained through reactions between organic precursors. Their structures are highly porous, stable and crystalline. Since COFs possess ordered, extended skeletons with uniform nanopores, the integration of functional groups is precise and can extend the field of applications for which this material may be used. There is evidence that organic semiconductor building blocks are able to retain their properties when integrated into a COF framework. COFs have applications in gas storage and separation, catalysis and energy storage.

HCPs are amongst the earliest of porous organic polymers and are generally prepared by post-crosslinking polystyrene-based precursors. A system of rigid building blocks fixed with strong covalent bonds maintains their highly porous structure. Their high cross-link density gives rise to their microporous structure. These materials have applications in gas sorption, heterogenous catalysis, drug delivery and chromatographic separation.

PIMs are a distinct class of porous materials in which the porosity does not arise from a network structure. They consist of linear macromolecular chains which do not pack efficiently. The packing is disturbed by the physical features of the monomers- in the case of PIM-1, contortion from the spirocentre and the rigid fused-ring structure- giving rise...
to microporosity. They are thermally stable and their synthetic reproducibility means that the reaction can be easily scaled. In the absence of a cross-linked 3D network, PIMs are solution processable, and their ultrahydrophobicity makes them a suitable choice for membranes for gas separation. They are also used in electronics.

PAFs are uniquely constructed from carbon-carbon-bond-linked aromatic-based building blocks. Their building units may be functionalised, or the materials may be designed for a specific application following post-modification of the aromatic motifs. They have extremely rigid and highly porous frameworks and have applications in gas adsorption and membrane separation.

Finally, CMPs are constructed of covalently bonded building blocks in a $\pi$-conjugated fashion. They exhibit high surface area and, unique to other POPs, conductive properties. The next section will introduce this material in more detail, its origin and the applications for which it can be used.

1.3 Conjugated Microporous Polymers

CMPs are a class of porous material which are semiconducting. They possess both $\pi$-conjugation and a permanently microporous skeleton. Conjugation arises from alternating single and double-/triple-bonds, connecting a system of p-orbitals with delocalised $\pi$-electrons which are able to bridge the single bonds. This property can be exploited in a number of applications, and is responsible for the rapid growth of interest since their discovery in 2007.

All CMPs are amorphous and generally possess microporosity, although some display micro- and mesoporosity. There are a large variety of building blocks which are available for the synthetic routes for these materials, rendering CMPs structurally diverse. Strong covalent bonding imparts thermal, mechanical and chemical stability. Yet, as with other porous materials with 3D networks, CMPs are insoluble in all organic solvents and takes their form as a powder.

1.3.1 Design and Synthesis Routes

CMP networks are formed through the reaction of two or more monomers or the homocoupling of one monomer. The most common approach involves the combination of a “core” molecule with a “linker” in coupling reactions which form C-C and C-N bonds.
Schiff-Base (S-B) condensation, Sonogashira-Hagihara, Suzuki-Miyaura, Yamamoto, oxidative coupling and Buchwald-Hartwig (B-H) amination are to name just a few reactions which can synthesise CMPs. Figure 1.9 outlines the aforementioned pathways, although this is not an exhaustive list of all possible synthetic routes.

For the purpose of selective CO$_2$ capture, B-H amination is a good choice, yielding nitrogen-rich CMPs. Figure 1.10 shows the catalytic cycle for B-H cross coupling. This particular reaction has been highlighted as it is used for CMP synthesis in this work. The reagents used in this facile synthesis have also been shown on the right of Figure 1.10.
The palladium (Pd) catalyst firstly forms a complex with the ligand (L). The oxidative addition step follows, in which the Pd inserts itself into the aryl halide (Ar-X). This results in an increase in the oxidation state and coordination number of the metal centre.

The amine co-ordinates with Pd via ligand exchange. The addition of the base (R”NaO) then removes the halide by deprotonation to give a Pd-N bond. Finally, the reductive elimination step decreases the oxidation state of the Pd centre whilst forming a new covalent bond between two ligands. This both regenerates the Pd-ligand complex for further reaction whilst also generating the aniline derivative (ArNRR’).

Many of the cross coupling reactions used for CMP synthesis are oxygen- and watersensitive, requiring anaerobic and/or anhydrous conditions to be employed. The difficulty of employing these conditions rigorously on a large-scale may preclude the scaled-up synthesis of CMPs. Furthermore, cross-coupling reactions make use of metal-based catalysts, predominantly Pd, which are expensive and may again preclude synthesis scale-up. In terms of applications, CMPs have a potential role in society as a material which can help with the global transition towards a greener future. Yet, their synthesis utilises...
metal catalysts which must be mined for, are difficult to recycle and known to be toxic.\textsuperscript{12} When assessing the life cycle impact of CMPs, their synthesis must be considered, and this should push towards the use of synthetic routes that utilise green chemistry.

There are many non-noble metal-catalysed reactions which can synthesise CMPs such as oxidative coupling, heterocycle linkages and S-B condensation. The latter two synthesise CMPs containing C-N bonds, making these materials appropriate for CO\textsubscript{2} capture, in a metal-free reaction.\textsuperscript{13} There is potential for “error-correction behaviour” in S-B condensation synthesis because of the reversibility of the imine bond formation.\textsuperscript{16} S-B condensation reactions are typically high yielding, and have synthesised CMPs with both high specific surface areas and CO\textsubscript{2} selectivity.\textsuperscript{84,85,97} A thiazolothiazole-linked CMP was synthesised by heterocycle linkaging and shows good selectivity of CO\textsubscript{2} over N\textsubscript{2}.\textsuperscript{94}

The choice of coupling reaction or synthetic route will affect the resulting properties of CMPs such as differences in polymer structure and semi-conducting behaviour.\textsuperscript{15} Solvent choice impacts the porosity; the first reported CMP networks were originally synthesised with toluene,\textsuperscript{83} but later testing revealed that changing the solvents and specific monomer combination could yield different levels of porosity.\textsuperscript{86}

This may be attributed to the Hansen Solubility Parameters (HSPs) of the CMP and the solvents used. The HSP theory dictates which solvents are designated as “good” and “bad” for a specific system according to the difference in the total solubility parameters of the solvent and the reaction product, $\delta_{T,\text{system}}$. The total solubility parameter, $\delta_T$, for a reagent is given in Equation 1.9:

$$\delta_T^2 = \delta_D^2 + \delta_P^2 + \delta_H^2$$  \hspace{1cm} (1.9)

$\delta_D$ is the HSP for dispersion interactions and is related to the molar volumes of the solvent, $\delta_P$ is for polar interactions and is caused by permanent dipole-permanent dipole interactions and $\delta_H$ is for hydrogen bonding, and results from interactions between molecules because of hydrogen bonds. The difference between $\delta_T$ for the solvent and CMP, for example, can be found using Equation 1.10.

$$|\delta_{T,\text{system}}| = |\delta_{T,CMP} - \delta_{T,\text{solvent}}|$$  \hspace{1cm} (1.10)

$\delta_{T,CMP}$ is $\delta_T$ for the CMP and $\delta_{T,\text{solvent}}$ is $\delta_T$ for the solvent. As a general rule that has
been followed for CMPs if $|\delta_{T,\text{system}}| < 1$, the solvent is a good choice. If $1 < |\delta_{T,\text{system}}| < 3$, the solvent is satisfactory and for $|\delta_{T,\text{system}}| > 3$, the solvent is a poor choice.

This hypothesis has been tested and shown to alter porosity of the CMP synthesised; using different solvents in reactions and testing the polymer/solvent compatibility, more suitable solvents for synthesis can be established, increasing yield and improving porosity. The addition of salts alters the HSPs of the solvent used, and has been used to tune the porosity of the CMP. Therefore, it is beneficial for researchers to spend time investigating optimal solvents and the addition of salts to improve yield and increase porosity when new materials are being prepared.

Furthermore, post-synthetic functionalisation can modify the properties of CMPs and improve their function for a particular application. The specific surface area, pore-volume and gas adsorption capacity of CMPs can change through the introduction or modification of functional groups. There are also examples where $\pi$-conjugated skeleton can be further adjusted by a postoxidation reaction.

The diversity of synthetic routes, tunability of CMPs and ability to post-synthetically modify, paired with $\pi$-conjugation and a permanently microporous skeleton, allows CMPs to be used for a wide range of applications, of which the most widely researched is gas separation and storage. CMPs have applications in the nuclear industry, capturing long-lived radioactive iodine isotopes such as $^{129}$I or $^{131}$I. Lithium-doped CMPs are a potential solution to the low-hydrogen-capacity issue faced by prospective materials for hydrogen storage. CO$_2$ is one of the most commonly reported gases for separation and storage by these materials, and there are many instances where N-rich CMPs show high selectivities for CO$_2$ over other gases (up to 360 CO$_2$/N$_2$ selectivity at 1 bar) and, in some cases, outperform other porous organic polymers.

Furthermore, due to their highly cross-linked network and their conjugated backbone, CMPs are ultrahydrophobic and are able to withstand moisture and harsh chemical and thermal environments. They offer thermal, chemical and moisture stability for the application of gas separation and storage which other candidates such as MOFs, zeolites and mesoporous silicas do not. However, at this point, it is not clear whether CMPs offer a particular advantage for gas capture and storage in terms of cost and processability over other materials. Therefore, the microporosity, $\pi$-conjugation and stability of these materials should be utilised in applications such as photoredox catalysis, light emittance,
supercapacitors and hydrogen evolution\textsuperscript{45} to make them truly advantageous over other prospective materials.

The next subsection introduces polyalnine and polyaniline-based CMPs. These are dopable, N-rich CMPs. The reason for this focus is because the CMP in this study is polyaniline-based. This opens the opportunities for these materials to be used for carbon separation and storage, and the possibility of the materials to be used for ECO\textsubscript{2}R.

\subsection{1.3.2 Polyaniline and Polyaniline-based CMPs}

The discovery of polyacetylene and its doping in the 1970’s led to widespread interest in conducting polymers\textsuperscript{108} Polyacryline (PANI) became a material of interest since then. PANIs are a class of conducting polymers synthesised from the oxidation of the monomer aniline. PANI is a homopolymer, but despite this, its structure may contain either benzenoid or quinoid (shown in Figure 1.11), or both at varying amounts\textsuperscript{109}.

![Figure 1.11: Aniline structures.](image)

PANI is synthesised using a chemical oxidant or by electrochemical synthesis and may be obtained in one of three oxidation states: leucoemeraldine (fully reduced) base (LB), emeraldine base (partially reduced) (EB) or pernigraniline (fully oxidised) base (PB)\textsuperscript{110}. The oxidation state of PANI is easily identifiable due to their colour, with LB being pale yellow, EB dark blue and PB violet\textsuperscript{110}. Therefore, PANI is used to describe this class of compounds of different oxidation states. The proportion of benzenoid (m) to quinonoid (n) may be tuned by the extent of oxidation and the synthetic route chosen. Different oxidation states have optimal m:n ratios:\textsuperscript{110}

- 1:0 for fully reduced LB
- 1:1 for partially reduced EB
- 0:1 for fully oxidised PB
PANI’s structure is shown in Figure 1.12 adapted from the thesis of Dr Pongsathon Boonrod, and the doping required to achieve different oxidation states.

![Figure 1.12: Oxidation, reduction and doping of PANI.](image_url)

The leucoemeraldine (LEB) and pernigraniline (PB) oxidation states are non-conducting, but the partially reduced emeraldine base (EB) may be acid-doped (unlike other conducting polymers of this class which rely on conventional redox doping), yielding the conductive emeraldine salt (ES, green in colour). This type of doping, known as p-doping, introduces electron holes (protons) into the polymer chain. The formation of a nitrogen base salt is responsible for the chemical stability of emeraldine salt PANI. The proton addition causes partial depopulation of the $\pi$-conjugated system which results in resonance, meaning all nitrogen atoms, C-N bonds and all C$_6$H$_4$ rings are identical. The ES form of PANI therefore possesses a highly conjugated $\pi$-system.

Keeping a balance between the benzenoid and quinonoid groups in the ES is required to achieve good electroactive performances. Irrespective of the synthesis method, the oxidation and reduction of PANI can be triggered chemically or electrochemically. PANI has a very distinct cyclic voltammogram in the region of -0.2 - 0.8 V (vs standard calomel
Introduction

electrode), which differ depending on the starting oxidation states. By far, the most stable and highest current-reaching oxidation state is that of the ES.\textsuperscript{112}

The redox activity and stability of PANI imparts many properties which may be exploited for a wide variety of applications. For example the ability of PANI to change colour on electrical input (changing between oxidation states) makes it a suitable materials for electrochromic windows.\textsuperscript{112} Its high specific capacitance, conductivity and various oxidation states make it suitable for supercapacitor electrode materials when used in conjunction with carbonaceous materials in composites.\textsuperscript{113} PANI may also be used in metal coatings in anti-corrosion applications because of its various oxidation states, resulting in its ability to passivate a metallic surface.\textsuperscript{115}

Due to its nitrogen-rich structure, PANI may be used for CO\textsubscript{2} separation and capture when grafted onto solid substrates such as graphene\textsuperscript{116} and MOFs.\textsuperscript{117} However, the need for a solid support and its PANI-modified surface introduces extra processing steps, likely increasing the processing time and cost of a scaled up version of this material. For this application, the development of CMPs structurally similar to PANI yields a nitrogen-rich, semi-conducting, microporous material. The material used in this study is called polytriphenylamine (PTPA) and is shown in Figure 1.4a. PTPA has already been shown to selectively capture CO\textsubscript{2}, and has future potential in catalysis and energy storage and conversion due to its extended \(\pi\)-conjugation.\textsuperscript{39,92}

This material has also been tested for the application of CO\textsubscript{2} capture and conversion. Previous work in the Faul research group has shown N-rich polymers to selectively capture CO\textsubscript{2} with a selectivity up to 360 over N\textsubscript{2} at 1 bar\textsuperscript{92} and convert it to more reduced chemical species, with product selectivity depending on the material’s pore size. The next section will introduce ECO\textsubscript{2}R, electrochemistry fundamentals and the materials used for this application.

1.4 Electrochemical CO\textsubscript{2} Reduction

1.4.1 Motivation for Electrochemical CO\textsubscript{2} Reduction

As already discussed in Section 1.1.2, electrochemical CO\textsubscript{2} reduction (ECO\textsubscript{2}R) is the conversion of CO\textsubscript{2} to more reduced chemical species, so has a direct application in the field of CCU in the global bid to prevent further climate change. Unlike many other capture
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techniques, ECO$_2$R provides economic incentive, generating valuable chemical feedstock from an unwanted by-product generated by many industries, from transportation to the industrial sector.$^{29}$

A variety of reduction products can be made: components of syngas such as carbon monoxide (CO) and methane (CH$_4$), or long-chain hydrocarbons, alcohols, oxygenates and olefins which, when produced by ECO$_2$R, act as sustainable fuel alternatives to gasoline. These value-added products provide an eco-friendly alternative to the production of starting materials used in industrial chemical synthesis (e.g. olefins for the production of plastics).$^{30}$

Alcohols produced by ECO$_2$R may be used as fuels in the transportation industry due to their compatibility with internal combustion engines (ICEs).$^{30}$ This both reduces emissions from this sector (once the alcohol is combusted, the CO$_2$ can be re-captured and reduced to fuels), and takes the pressure off of the electric vehicle (EV) industry. This allows time for EV technology to mature, EV costs to reduce and charging infrastructure to improve.$^{118}$ ECO$_2$R therefore supports a just climate transition, supporting communities for which cutting-edge EV-technology is not yet accessible.

Finally, ECO$_2$R brings forward a way to reliably store renewable energy. The intermittency of wind and solar energy presents many challenges in terms of long-term energy storage. However, when powered by these intermittent forms of energy, ECO$_2$R can provide a way to convert electrons generated by renewable power into stable chemicals (i.e. fuels) in a form of long-term energy storage.$^{63}$

This technique can clearly be implemented to aid a global transition to a low-carbon economy, so is a process which has received years of intensive research in order to industrialise it. However, ECO$_2$R is a kinetically-slow process due to the chemical stability of CO$_2$, requiring specially-designed catalysts and reactors to achieve industrial benchmarks (Table 1.4).$^{29,119}$ Often, the input of large amounts of electrical energy, larger than that of the reaction’s half potentials, are required for a reaction to take place. Therefore, the development of suitable electrolytes, catalysts and electrochemical reactors is necessary to commercialise ECO$_2$R. The following section will introduce the chemistry of CO$_2$ reduction and areas which require improvement.

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1.4.2 Chemistry of CO$_2$ Reduction

Electrochemistry is the study of chemical changes caused by the passage of electrons and subsequent production of electrical energy in some cases. These electron-transfer processes, or redox reactions, typically involve electrons moving between electrodes via electronically- or ionically-conducting phases. Electrochemical measurements are made for a number of reasons, for example obtaining thermodynamic data about a reaction, generation of unstable reaction intermediates for further study or to test for trace metal ions or organic species in a material.

Cyclic voltammetry (CV) is a powerful electrochemical technique employed to investigate the oxidation and reduction processes of molecules and may be used for the aforementioned measurements. The technique applies a potential difference to the system, which sweeps linearly back and forth between two pre-defined potentials and the resulting current is measured. The voltage applied is in excess of that predicted by the Nernst equation (Equation 1.11).

\[
E = E^0 + \frac{RT}{nF} \ln \left( \frac{(Ox)}{(Red)} \right) = E^0 + \frac{RT}{nF} \ln \left( \frac{[Ox]}{[Red]} \right) \tag{1.11}
\]

E is the potential of the electrochemical cell and $E^0$ is the standard potential of a species. F is Faraday’s constant (96,385 C/mol), R is the universal gas constant, n is the number of electrons transferred in the reaction and T is the temperature in kelvin. (Ox), (Red), [Ox] and [Red] are the activities and concentrations of the oxidised and reduced species respectively. Solids in electrochemical cells have an activity of 1 and for liquid species, the concentration is a close approximation to their activities.

This equation can be used to explain the presence of peaks seen in cyclic voltammograms, which indicate reduction or oxidation of chemical species within the electrochemical cell due to increased electron flow, and thus an increase in current. For example, during reduction, a chemical species is gaining electrons, resulting in an increase in the cathodic current measured. This will increase the concentration of the reduced species, meaning E tends to negative values. During oxidation, a chemical species is losing electrons, resulting in an increase in the anodic current measured. This increases the concentration of the oxidised species so E tends to more positive values.
In terms of $\text{ECO}_2\text{R}$, this is an important technique. For example, performing CV over a number of cycles indicates material stability; if current values continually decrease over a number of cycles then this may suggest material degradation. If peak-to-peak separation ($\Delta E_p$) is 57 mV, then the reaction is reversible, again denoting stability.\cite{121}

$\text{ECO}_2\text{R}$ tests are commonly conducted in Ar- and $\text{CO}_2$-saturated electrolyte. Changes in current between CV conducted in Ar and $\text{CO}_2$ indicate catalyst interaction with $\text{CO}_2$, whether it be an increase\cite{122,123} or decrease\cite{124,125} in the current between the Ar and $\text{CO}_2$ voltammograms.

The comparison of cyclic voltammograms conducted in Ar and $\text{CO}_2$ helps to assign peaks to the oxidation and reduction of the catalyst or to hydrogen evolution. $\text{CO}_2$ reduction peaks present in the cyclic voltammograms can therefore be distinguished\cite{122,123,124,125}. Knowing these potentials is useful for the purpose of producing the reduction products by chronoamperometry.

Chronoamperometry (CA) is a time-dependent electrochemical technique where a step potential is applied to the working electrode. The current the electrode maintains is a function of time. CA is a good technique to describe diffusion of an analyte from bulk solution. Performing CA with a catalyst for aqueous $\text{CO}_2$ reduction is a good way to identify reduction products after collecting the electrolyte and performing nuclear
magnetic resonance (NMR) spectroscopy for analysis.

There are other electrochemical techniques which may be deployed to characterise liquid and gaseous reduction products. In-situ techniques such as differential electrochemical mass spectrometry (a type of mass spectrometry technique which allows for mass-resolved determination of gaseous electrochemical reaction products) may be used in conjunction with CV. However, the aforementioned process which utilises NMR spectroscopy must be coupled with chronoamperometry and is the method employed in this study.

ECO$_2$R routes can be realised through the adsorption of CO$_2$ onto catalyst active sites and multiple proton-electron transfer reactions in aqueous media. Test set-ups consist of a working electrode (WE) where either CO$_2$ reduction or the hydrogen evolution reaction (HER, highlighted in blue in Table 1.3) occurs, a reference electrode (RE, an electrode with a constant potential, used to reference the working electrode’s potential against) and a counter electrode (CE), which balances the current generated at the working electrode by the oxygen evolution reaction (OER, highlighted in yellow in Table 1.3). The catalyst for ECO$_2$R are typically nanoparticles, and are deposited onto a conductive support such as carbon paper, glassy carbon or metal foils and bound using an ion-conducting binder.

Fundamental aqueous-phase reactor studies (shown in Figure 1.14) are initially conducted to identify promising materials for this application, before they are tested in vapour-fed electrochemical reactors (to be discussed later in this section).

![Figure 1.14: Aqueous-phase reaction set up, with possible reduction pathways occurring on catalyst surface.](image)

Aqueous-phase reactors consist of a cell split by an ionically-conducting membrane
(ICM), to prevent oxidation of any reduction products produced at the WE by the CE. The WE, RE and CE are immersed in an aqueous electrolyte, with the cathodic side of the cell being purged with either CO$_2$ or Ar. All electrodes are connected to a potentiostat, which controls the electrochemical reaction.\cite{131} Figure 1.14 shows one of many possible ECO$_2$R pathways. It also shows that hydrogen evolution occurs at the catalyst surface, and how hydrogen adsorption blocks active sites for CO$_2$ adsorption and reduction.

The reduction pathway in Figure 1.14 shows one of many possible reduction products (formic acid). There are also multiple reaction pathways for a single reduction product, depending on the pH of the electrolyte and catalyst used. For example, there are two proposed mechanisms for the production of methano\cite{132} which have a CO or HCOO$^-$ intermediate. Even different types of metals reduce CO$_2$ selectively to different products, and via different pathways.\cite{133,134}

All possible pathways and interaction mechanisms start with the formation of the bent radical ion CO$_2$·$^-$ from the linear, chemically stable CO$_2$ molecule.\cite{133–135} During this process, the C=O bond is strongly perturbed and electrons are shared between the catalyst and CO$_2$.\cite{136} This step requires the highest potential of any half-reaction occurring at the working electrode, and is generally responsible for the electrical overpotential (the added potential to the half-reaction potential) required to drive the cathodic half-reaction.\cite{135}

Despite the added electrical energy to the system, ECO$_2$R still competes with the HER. In this reaction, hydrogen is produced by the electrolysis of water, with the OER continuing to occur at the counter electrode. Its standard potential is comparable with that of many CO$_2$ reduction reactions, so it is important the catalyst suppresses H$_2$ formation whilst simultaneously promoting ECO$_2$R. Table 1.3 shows some of the half-reactions, and their potentials against the standard hydrogen electrode (SHE) at pH 7.
Table 1.3: Some half-reactions occurring at the anode and cathode during ECO$_2$R. OER potential vs SHE at pH = 7: 0.8 V, HER potential vs SHE at pH = 7: -0.4 V.

<table>
<thead>
<tr>
<th><strong>Oxygen Evolution Reaction (OER)</strong></th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$</td>
<td>pH &lt; 7$^{137}$</td>
</tr>
<tr>
<td>$4OH^-(aq) \rightarrow O_2(g) + 2H_2O(l) + 4e^-$</td>
<td>pH &gt; 7$^{137}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Hydrogen Evolution Reaction (HER)</strong></th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2H^+(aq) + 2e^- \rightarrow H_2(g)$</td>
<td>pH &lt; 7$^{137}$</td>
</tr>
<tr>
<td>$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$</td>
<td>pH &gt; 7$^{138}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>ECO$_2$R Reactions</strong></th>
<th>Potential vs SHE pH = 7 (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CO_2(g) + e^- \rightarrow CO_2^-(aq)$</td>
<td>-1.90$^{129}$</td>
</tr>
<tr>
<td>$CO_2(g) + 2H^+(aq) + 2e^- \rightarrow HCOOH(l)$</td>
<td>-0.61$^{129}$</td>
</tr>
<tr>
<td>$CO_2(g) + H_2O(l) + 2e^- \rightarrow HCOO^-(aq) + OH^-(aq)$</td>
<td>-0.43$^{129}$</td>
</tr>
<tr>
<td>$CO_2(g) + 2H^+(aq) + 2e^- \rightarrow CO(g) + H_2O(l)$</td>
<td>-0.53$^{129}$</td>
</tr>
<tr>
<td>(C) $CO_2(g) + H_2O(l) + 2e^- \rightarrow CO(g) + 2OH^-(aq)$</td>
<td>-0.52$^{129}$</td>
</tr>
<tr>
<td>$CO_2(g) + 6H^+(aq) + 6e^- \rightarrow CH_3OH(l) + H_2O(l)$</td>
<td>-0.38$^{129}$</td>
</tr>
<tr>
<td>$CO_2(g) + 5H_2O(l) + 6e^- \rightarrow CH_3OH(l) + 6OH^-(aq)$</td>
<td>-0.81$^{129}$</td>
</tr>
<tr>
<td>$2CO_2(g) + 7H^+(aq) + 8e^- \rightarrow CH_3COO^-(aq) + 2H_2O(l)$</td>
<td>-0.26$^{129}$</td>
</tr>
</tbody>
</table>

A key challenge to improve the efficiency of ECO$_2$R is the low solubility (35 mmol/L) of CO$_2$ in water under standard conditions (atmospheric pressure and room temperature). This leads to a low limiting current density for ECO$_2$R for aqueous-based systems, taking values as low as 20 mA/cm$^2$. Limiting current densities arise because electrochemical processes are diffusion-limited.$^{130}$

As ECO$_2$R begins, the current supplied by the WE will increase as the potential applied to the system is increased. The solution surrounding the WE will be depleted of the reducing agent, CO$_2$, corresponding to a maximum current at which CO$_2$ will be reduced. At this point, the reaction is mass-transport limited. The diffusion of CO$_2$ to catalyst adsorption sites is insufficient so HER takes place instead.$^{131}$

Several methods have been proposed to overcome this limiting current, from increasing the pressure of the system to decreasing its temperature. Careful electrolyte choice can
decrease local pH effects on CO$_2$ content. The dissolution of CO$_2$ in aqueous media is as follows:\textsuperscript{140}

\[ CO_2(g) \rightleftharpoons CO_2(aq) \quad (1.12) \]

\[ CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \rightleftharpoons 2H^+(aq) + CO_3^{2-}(aq) \quad (1.13) \]

The increase in H$^+$ concentration with CO$_2$ dissolution increases the likelihood of the HER occurring. H$^+$ ions at the electrode surface are consumed until the area immediately surrounding the electrode is depleted, so H$_2$O is reduced to produce H$_2$ instead (reaction shown in Table 1.3). This increases the content of OH$^-$ surrounding the electrode, pushing the equilibrium in Equation 1.13 to the right, decreasing the content of electrochemically-active CO$_2$ surrounding the electrode.\textsuperscript{141,142}

Work has been done to exploit the superior conductivity of acidic electrolytes for ECO$_2$R. In this case, OH$^-$ ions generated by half-reactions occurring at the WE react with H$^+$ ions in the electrolyte, producing water.\textsuperscript{143} Ionic liquids (ILs) are also being used as electrolytes for ECO$_2$R, due to their high CO$_2$ absorption capacity and their ability to stabilise charged CO$_2$ species.\textsuperscript{143,144} However, high-cost and viscosity means that industrial IL-based ECO$_2$R reactors have not yet been realised.\textsuperscript{143}

An aqueous electrolyte with a high pH will shift the equilibrium of Equation 1.13 towards the right, reducing the content of electrochemically active CO$_2$ in solution. Carbonate-based electrolytes such as potassium hydrogen carbonate (KHCO$_3$) have the ability to act as a buffer. They dissociate to produce a bicarbonate ion, disturbing the equilibrium reaction in equation 1.13, potentially increasing the amount of CO$_2$ in solution.\textsuperscript{145}

\[ KHCO_3(s) \rightleftharpoons K^+(aq) + HCO_3^-(aq) \quad (1.14) \]

The bicarbonate buffer also neutralises OH$^-$ ions at the electrode surface,\textsuperscript{146} preventing the equilibrium shift of Equation 1.13 to the right. This maximises aqueous, electrochemically active CO$_2$ in solution.\textsuperscript{145,147}

\[ HCO_3^-(aq) + OH^-(aq) \rightleftharpoons H_2O(l) + CO_3^{2-}(aq) \quad (1.15) \]
However, some findings show that changes in pH at the cathode surface are too small to result in any buffering effects\textsuperscript{138}, whereas another study suggests that as CO\textsubscript{2} is consumed in ECO\textsubscript{2}R at the electrode surface, a different equilibrium is established. Here, the electrolyte bicarbonate anion can act as a form of CO\textsubscript{2} itself, shown in equation (1.16).

\[ HCO_3^- (aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^- (aq) \rightleftharpoons CO_2(aq) + H_2O(l) + OH^- (aq) \]  

(1.16)

It is also suggested that bicarbonate buffering anions act as a source of hydrogen for the HER and that to maximise the yields of multi-carbon products whilst minimising \( H_2 \) production, electrolytes of low buffering capacity should be used\textsuperscript{138}. The choice of electrolyte cation and anion has an obvious effect on ECO\textsubscript{2}R, but more work has to be done to gain a full understanding of the impact. Despite this, weakly buffering electrolytes of low salinity, such as 0.1 M KHCO\textsubscript{3}, have been identified as a good medium for which ECO\textsubscript{2}R to occur, maximising product formation\textsuperscript{138}.

Even with the careful choice of electrolyte and specially designed catalysts, aqueous-phase reactor designs could never reach industrial-scale requirements for ECO\textsubscript{2}R due to low current densities reached by these simple immersion-based techniques. Electrolysers for ECO\textsubscript{2}R are a more attractive type of reactor, and are now beginning to reach pilot scale\textsuperscript{138}. ECO\textsubscript{2}R to CO is perhaps the closest of all reaction pathways to commercialisation. Table 1.4 (adapted from Masel et al.,\textsuperscript{119} and De Luna et al.,\textsuperscript{31}) defines the industrial benchmarks for CO\textsubscript{2} reduction to CO, which are achievable values with the use of vapour-fed CO\textsubscript{2} electrolysers.

Table 1.4: Industrial benchmarks for CO\textsubscript{2} reduction to CO\textsuperscript{119,119}

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Industrial Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyser current density</td>
<td>200 - 500 mA/cm\textsuperscript{2}</td>
</tr>
<tr>
<td>Catalyst activity</td>
<td>100 A/g</td>
</tr>
<tr>
<td>Voltage increase at constant current</td>
<td>10 ( \mu )V/h</td>
</tr>
<tr>
<td>Cost of CO produced</td>
<td>$700/tonne CO</td>
</tr>
<tr>
<td>Faradaic efficiency</td>
<td>95%</td>
</tr>
</tbody>
</table>

The current density is an important parameter, describing the current the catalyst
can supply to ECO$_2$R independent of its surface area. The catalyst activity describes the amount of current that should be passing through the catalyst per gram of material. The voltage increase at constant current is also an important parameter describing the long-term efficiency of the catalyst. Catalysts are now able to support CO$_2$ reduction to CO for up to 3,800 hours at a constant current, with only a 10 mV increase in potential supplied. Catalysts which require potential increases larger than 10 $\mu$V/h are too energy inefficient for an industrially scaled process.

The product generated must be at least the same cost that other suppliers sell the chemical for ($700/tonne CO). The main cost of ECO$_2$R is the price of electricity to operate the process, so electrochemical reactors need to operate at high energy conversion efficiencies to achieve or excel this value. The Faradaic efficiency (FE) describes the efficiency with which electrons are transferred by a catalyst supporting an electrochemical reaction. Since there are many possible reaction products, and reaction pathways generally requires multi-electron/proton transfer, FEs for ECO$_2$R are typically low. However, for industrially-scaled processes, near-100% FEs are necessary to maximise the energy efficiency of the process. Equation 1.17 is used to calculate FE.

$$FE = \frac{nF\eta}{Q}$$

n is the number of electrons transferred in the reaction for a specific reduction product, F was defined in equation 1.11 and Q is the total charge accumulated in the system, determined by chronoamperometry and $\eta$ is the amount of product produced in mol.

The standards in Table 1.4 are achievable using vapour-phase electrolysers. In these reactors, the catalyst for ECO$_2$R is deposited with micro- to nanometre thickness onto a hydrophobic, microporous support on one side of a gas diffusion layer (GDL). CO$_2$ is then passed over the hydrophobic, microporous support and the electrolyte is passed over the thin catalyst layer, on the other side of the GDL.

During operation, the porous catalyst layer is fully covered by the electrolyte whilst CO$_2$ diffuses across a gas-liquid interface maintained by the hydrophobic surface of the microporous layer. It is assumed that CO$_2$ travels a short distance through the microporous layer, dissolves in the electrolyte and is reduced in a three-phase solid-liquid-gas interface.
It is essential to prevent flooding of the GDL to maintain a stable gas-liquid equilibrium. If this occurs, the diffusion distance CO₂ must travel to reach the catalyst increases and the process is once again mass-transport limited, decreasing achievable current densities. Without flooding of the GDL, CO₂ only has to diffuse from a nearby gas phase through the microporous, hydrophobic layer. The catalyst and catholyte are constantly replenished with CO₂ and large electrochemically active areas are achievable, meaning aforementioned industrial benchmarks are possible.

In other chambers of the electrolyser sit the RE and CE. The CE is separated from the catholyte by an ion-exchange membrane (either an anion-, proton- or bipolar-exchange membrane), with the anolyte flowing behind this GDL. Figure 1.15 shows a gas-diffusion electrolyser (GDE) set up.

Figure 1.15: GDE set up.

GDEs taking the form in Figure 1.15 still require a reduction in reaction overpotential. This means that the conductivity of the electrolyte should be increased and the distance between the anode and cathode decreased, minimising ion-transport limitations. Membrane-electrode-assemblies (MEAs) satisfy these two requirements by removing the
aqueous electrolyte entirely, and ionically connecting the anode and cathode by an ionomer (ion-conducting polymer). Membranes used in these systems are typically on the order of 10 to 100 µm thick with high conductivities.\textsuperscript{[60]}

Despite the clear advantage to these vapour-phase electrochemical reactors over traditional H-cell setups, the vast amount of literature for cutting-edge catalysts for ECO$_2$R have been conducted in the less-efficient, aqueous-phase reactors. This poses an important question: how representative are the conclusions from these aqueous-fed systems, that are constrained to low current densities, when it is well known the energetics of a reaction occurring on a catalyst’s surface are highly sensitive to changes in reaction rate? There has been a recent shift in research into using catalysts in, and advancing materials for, GDEs as ECO$_2$R reaches industrialisation since these testing conditions are more commercially relevant.\textsuperscript{[141,150]}

Needless to say, aqueous-phase reactors are still a robust method for identifying promising catalysts for ECO$_2$R before further study in GDEs, and the H-cell set up is employed in this study. The next section will discuss these promising materials, and introduce CMPs as a potential catalyst for the application of CO$_2$ reduction.

1.4.3 Materials for Electrochemical CO$_2$ Reduction

Subsection 1.4.2 discusses some of many possible reduction products that may be formed and introduces the idea of different reaction pathways to arrive at the same product. As aforementioned, the only reduction pathway close to commercialisation is CO$_2$ to CO, and in general, ECO$_2$R is limited to C1 to C3 chemical products.

State-of-the-art catalysts are limited to C$_1$ to C$_3$ products for two main reasons: firstly, higher carbon species require more proton-electron transfer reactions, leading to highly complex reaction pathways and poor product selectivity. Secondly, as the number of electrons transferred increases, the energy conversion efficiency of the process decreases. Catalysts should be designed to reduce the effects of, or even negate, these process limitations. They should:

- Show selectivity for ECO$_2$R over HER, demonstrating good catalyst activity.
- Maintain high current densities.
- Remain stable over an industrially-relevant number of cycles.
• Be abundant and low-cost.

• Neither bind too strongly or too weakly to reaction intermediates.

• Have less negative onset potentials.

• Reduce CO₂ at low overpotentials.

• Have high turnover frequencies (the reaction turnover per catalytically active site).

• Show high product selectivity.

• Have a high electrochemically-active surface area.

• Be easily processable.

Metal Catalysts

Metals are of the most researched catalysts for ECO₂R. They have the ability to reduce CO₂ to a variety of products, and are categorised depending on the reduction product they produce and the reaction pathway this is done by. Table 1.5 illustrates this.

Table 1.5: Classification of metal catalysts for ECO₂R.

<table>
<thead>
<tr>
<th>Group</th>
<th>Metals</th>
<th>Main Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Sn, Pb</td>
<td>Formate, formic acid</td>
</tr>
<tr>
<td>II</td>
<td>Au, Ag, Pd, Zn and Bi</td>
<td>CO</td>
</tr>
<tr>
<td>III</td>
<td>Cu</td>
<td>Formate, CO, hydrocarbons, alcohols</td>
</tr>
</tbody>
</table>

The groups are defined on whether product formation proceeds through an oxygen-bound (-OCHO) or carbon-bound (-COOH) reaction intermediate, which may then form formate/formic acid and CO respectively. Density function theory (DFT) calculations and experimental evidence has shown that the oxophilicity of metal catalysts determines these reaction intermediates. Therefore, the low oxophilicity of noble metals such as Ag and Au tend to bind to the carbon-bound intermediate, producing CO, whereas Sn catalysts bind to the -OCHO intermediate, producing formate/formic acid.

Although much work has been put into designing metal catalysts for ECO₂R, the products most commonly formed are CO and HCOO⁻, and most catalysts struggle to reach the industrial standards required for the most simple 2e⁻ reactions of ECO₂R.
In a group of its own, Cu is the only catalyst which consistently converts CO$_2$ to C$_{>1}$ products.$^{134}$

It is generally accepted that Cu begins most reduction pathways via the carbon-bound intermediate $\cdot$COOH$^{135}$ (HCOO$^-$ formation by the oxygen-bound intermediate $\cdot$OCHO is possible, but not the dominant method of production since Cu-$\cdot$OCHO binding is weak$^{152}$). The formation of CO is a key intermediate for the formation of hydrocarbons$^{153}$ and alcohols$^{153}$ in ECO$_2$R. However, Cu catalysts demonstrate poor product selectivity and activity degradation.

To enhance reaction rates and prevent catalyst degradation, metal catalysts may typically be metal oxides, organometallics, metal alloys and metal carbides. The variety of forms metal oxides can take has the advantage of tuning the binding capabilities of radical reaction intermediates. The incorporation of other species into metal catalysts also brings down catalyst costs.$^{129}$

For example, bismuth oxide nanocatalysts (e.g. Bi$_2$O$_3$, Bi$_2$O$_2$O$_3$) are the most industrially relevant materials for ECO$_2$R to formate.$^{112}$ Specially designed metal alloys can produce hydrocarbons at low overpotentials.$^{154}$ Tungsten carbides may be coated with transition metals, altering the oxo- and carbophilicity of the surface and therefore the binding energies to reaction intermediates.$^{155}$ There are clearly many opportunities to successfully tune metal catalysts to selectively reduce CO$_2$ to specific products.

Catalyst morphology also impacts ECO$_2$R, and metal catalysts are most often in the form of nanocatalysts (supported by carbon conductive supports such as glassy carbon), as this increases the electrochemically-active surface area.$^{129,134}$ Surface modification can alter the surface energy and surface-atom oxidation states of the metal. This also changes external factors such as local pH gradients and the mass-transport of CO$_2$ molecules.$^{156}$

For example, well-established metal processing techniques such as work hardening may be used to introduce bulk lattice defects such as grain boundaries into metal catalysts. This has enhanced CO$_2$ reduction to CO on Au catalysts.$^{157}$ Steep pH gradients were observed on a Cu foil surface supporting Cu nanowires; the nanowire length and density could be changed, preventing anion diffusion to the electrode surface to enhance hydrocarbon and alcohol formation.$^{158}$

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However, despite careful design, surface modifications do not always translate to long-term stability, since the surfaces can deteriorate by dissolution, agglomeration and coalescence. Furthermore, metal catalysts are often costly, and their surfaces can become contaminated by metal impurities present in many salts used in aqueous-based electrolytes, interfering with complex electron-proton transfer reactions and selectivity of $\text{ECO}_2\text{R}$ over HER. Catalysts which show strong binding for specific reaction intermediates may suffer from surface poisoning, in which catalytically active sites are blocked for further $\text{CO}_2$ adsorption.

### Metal-free carbon-based catalysts

Metal-free catalysts do not suffer from surface deactivation and generally show better catalyst stability in comparison to metal catalysts. They are also attractive materials for $\text{ECO}_2\text{R}$ as they offer a low-cost alternative to expensive metals for $\text{ECO}_2\text{R}$.

Scaling relations describe the inability to tune the adsorption energy of one reaction intermediate without others. This has plagued metal catalysts with high overpotentials because $\text{ECO}_2\text{R}$ has multiple electron/proton transfer reactions and often, more than one reaction intermediate. d-states are responsible for the change in adsorbate-metal interaction energies and since carbonaceous materials do not possess any d-band features (only sp states, which show identical interaction with reaction intermediates), they are not subjected to the implications of scaling relations.
As before, CO$_2$ reduction begins with the formation of the radical CO$_2$·. Reduction may take place with the formation of the -COOH or the -OCHO intermediates, and depends on the morphology of the carbon catalyst. For example, graphene-based catalysts produce CO and formic acid through the -COOH whilst carbon nanotube catalysts may activate CO$_2$ through either intermediate.

The pore structure of carbonaceous catalysts can be tuned to alter the diffusion of solvated reaction species to increase reaction rates, but without heteroatom-doping, carbon catalysts are electrochemically inert in terms of ECO$_2$R due to their inability to adsorb CO$_2$ and other reaction intermediates. Doping effectively modifies the local electronic structure, introduces structural defects and induces surface charge polarisation.

N-doping is the most common type of heteroatom doping and gives rise to 3 N configurations: pyridinic, pyrrolic and graphitic N as shown in Figure 1.17. There is both experimental and theoretical evidence demonstrating that pyridinic N acts as the active site for CO$_2$ reduction reactions due to its accessible lone electron pair.

Figure 1.17: Nitrogen configurations in N-doped carbonaceous species.

Perhaps because N-doped carbon catalysts are of the most researched metal-free catalysts for ECO$_2$R, there are many different morphologies reported in literature such as N-doped carbon nanotubes and nanofibers, graphene, nanodiamonds and mesoporous carbons. N-doped carbonaceous materials are often used as carbon supports for metal catalysts in ECO$_2$R as they can assist adsorption and desorption of reaction intermediates. However, carbon-based catalysts have exceeded many metal catalysts in their ability to reduce CO$_2$ selectively to C$_{\geq1}$ products at moderate overpotentials.
For example, N-doped mesoporous carbons with an ordered cylindrical structure could reduce CO\textsubscript{2} to ethanol at moderate overpotentials with high FEs (77%), requiring C-C coupling (a reaction feature which evades many metal catalysts).\textsuperscript{164} Electropositive B can be used as a dopant in diamond catalysts\textsuperscript{159} to reduce CO\textsubscript{2} to formaldehyde at high FEs (74%), which is scarcely reported as a reduction product at such high reaction rates.\textsuperscript{165}

F-, S- and P-doping are other possible doping atoms, but more work needs to be done in this area.\textsuperscript{135,159} Co-doping is another possibility, bringing unprecedented charge distribution and electronic structure which may be responsible for the reduction of CO\textsubscript{2} to ethanol at moderate overpotentials and high FEs (93.2%) by B,N-doped nanodiamonds.\textsuperscript{166}

Despite good activity, there is controversy about the presence of trace metals in carbonaceous catalysts which are hard to remove, and the contaminant’s impact on ECO\textsubscript{2}R.\textsuperscript{135} It is possible that these metal impurities enhance reaction rates, meaning product formation may not arise from these carbonaceous materials alone.\textsuperscript{156}

MOFs have gained increasing popularity as starting precursors for metal-nitrogen-carbon catalysts, which are a metal/carbon hybrid catalyst for ECO\textsubscript{2}R. However, MOFs are emerging as a class of material in their own right for ECO\textsubscript{2}R.

**Metal Organic Frameweworks**

MOFs have recently received an increased interest in the field of catalysis.\textsuperscript{167} Improved mass transport, which has previously plagued ECO\textsubscript{2}R processes with low reaction rates, is seen with MOFs owing to their high surface areas. As described in Subsection 1.2.3, their chemical and structural tunability is unprecedented and may be used beyond gas capture to alter properties such as conductivity and selectivity to improve the ECO\textsubscript{2}R process.\textsuperscript{168}

MOFs may be used as catalysts for ECO\textsubscript{2}R in their pristine form, with the active sites either on their metal nodes or organic ligands.\textsuperscript{167} The latter is the case for Zn-based MOFs, whose metal centres do not partake in the ECO\textsubscript{2}R process due to a fully occupied d-orbital in the Zn\textsuperscript{2+} oxidation state.

ZIF-8’s (a zeolitic imidazolate framework), ligands were doped with a strong electron donor, which was shown to lower energy barriers for the formation of the key intermediate -COOH, facilitating CO production with a FE of 90.57%.\textsuperscript{169} The dopant also negated the need for a conductive support, which are commonly required by MOF electrocata-
The metal centres may also be chosen to tune the reduction process. The properties of some metals to reach many oxidation states, such as Co, Fe and Cu, can be exploited to catalyse the ECO\textsubscript{2}R process. Electrons arising from metal centres reaching different oxidation states can assist in the electron transfer reactions in ECO\textsubscript{2}R and has even helped to achieve C-C coupling.

MOFs are also good catalyst supports owing to their high surface area structure, increasing the activity of metal catalysts than if they were to be used alone. As aforementioned, MOFs may also be used as precursors for the production of electrocatalysts, again yielding good catalyst dispersion in a high surface area structure, increasing electroactivity of the catalysts.

Finally, MOFs may also be used in composites. For example, Au nanostructured microelectrodes were shown to be suitable surfaces for the growth of various different MOFs. During ECO\textsubscript{2}R, CO\textsubscript{2} was reduced to CO, as is commonly the case for Au catalysts, but this was followed by further reduction of the \cdot CO intermediate in the pores of the MOF to generate methane and ethene, completely suppressing CO generation.

The fact that different electrocatalysts and their individual properties for ECO\textsubscript{2}R can be used in tandem with one another to better the process presents an exciting concept. MOFs are not only an interesting electrocatalyst for ECO\textsubscript{2}R, but have also been helpful in providing understanding of the relationship between the structure and properties of catalysts and ECO\textsubscript{2}R at a molecular level. Extensive literature has provided insight of how tuning their metal nodes and linkers can alter ECO\textsubscript{2}R.

However, as a newer material for this application, there are few examples of where MOFs are used as catalysts for ECO\textsubscript{2}R in electrolysers and it is important to test these materials in more commercially-relevant conditions. Furthermore, long-term stability of MOFs has presented issues in the field of gas capture, and there are few studies which evaluate MOF stability post-ECO\textsubscript{2}R.

**Conjugated Microporous Polymers**

Owing to their photocatalytic activity, there are many studies reporting CMPs as photocatalysts for photocatalytic CO\textsubscript{2} reduction, in which photocatalysts harvest light as the energy input for the reaction to occur. Whilst a promising method, photocatalytic
CO$_2$ reduction requires more work to reach industrialisation [42][177].

MOF- and COF-based materials for ECO$_2$R typically contain molecular electrocatalysts within the framework, providing electrode materials with stable, well-defined and tunable catalytic sites. CMPs have also been known to act as supports for such electrocatalysts. The OER[178][181] and oxygen reduction reaction[182] has been catalysed by Co-CMPs, showing good electrochemical reactivity towards the reactions, reducing catalyst agglomeration and improving mass transport within the porous structure. The $\pi$-conjugated framework of CMPs also allows for delocalisation of charge between catalytic sites[178][181][182].

CMPs have been used as supports for electrocatalysts for ECO$_2$R in which metal nanocatalysts and complexes are immobilised into CMP frameworks, producing CO[183][184] and in some cases some higher chain reduction products[185][186] (although these products were observed at higher reaction temperatures and pressures). Whilst these metal-CMP hybrid catalysts show good activities for CO$_2$ reduction owing to the stability and porosity of CMP structures, the extra processing step of immobilisation is likely to increase catalyst cost.

PTPA is a CMP which may be used for ECO$_2$R, but does not require the immobilisation of electroactive moieties to achieve good electroactive performance. N atoms throughout the N-rich polymer act as electroactive sites in a way similar to those in N-doped carbonaceous materials, with the interaction mechanism described in Section 1.1.3. However, it is clear that research into CMP-based catalysts for ECO$_2$R is lacking. The large majority of published literature is based on metal catalysts. This implies that the current knowledge of reaction pathways and factors influencing ECO$_2$R may not apply to CMPs. However, the current knowledge could be used to design CMPs and alter porosity and morphology to achieve catalysts with good activities for ECO$_2$R.

Furthermore, to remove the energy-intensive CO$_2$-stripping processes from solvent-based CO$_2$ capture, direct electrolysis of CO$_2$ in these capture sorbents is being researched as a possibility. However, amine-based liquid sorbents, the most commonly used industrial CO$_2$ capture media, are corrosive to metals[187]. Owing to their stability, CMP electrocatalysts may be more suitable, providing a solution to the high cost of solvent regeneration and potential electrocatalysts for this application.
Furthermore, CMPs have the potential to entirely replace current industrial capture sorbents because of their thermal and chemical stability, and then be used directly as catalysts for ECO$_2$R. However, because of their conjugated systems, CMPs in their as-synthesised forms are non-solution-processable powders. Incorporating these materials into a solution-processable support presents an attractive alternative to using these materials industrially.

1.5 3D Printing

3D printing, a type of additive manufacturing (AM), is a technique which allows for fast prototyping of both simple and complex 3D structures from a wide variety of precursor materials. The structures are produced through a layer-by-layer process, generally controlled by computer-aided design (CAD) software. The process has found applications in many industries from construction to the fabrication of medical devices because AM is scalable, allows high levels of control over the processing of complex structures and reduces material waste, costs and manufacturing time.\textsuperscript{188}

In recent years, 3D printing has gained interest for the fabrication of electrodes for electrochemical reactors and even the reactors themselves. Many solid-state materials previously discussed in Sections 1.2.3 and 1.4.3 have unique features making them suitable for adsorptive and catalyst activity, but because many exist naturally as powders, their practical form must be modified for industrial application.\textsuperscript{189}

As an example, PTPA in its powdered form for industrial CO$_2$ capture and conversion would be difficult to control at industrial flow rates, making the collection of PTPA for ECO$_2$R difficult and material losses highly likely. Some processing techniques can form powdered materials into pellets or granules, but this can result in material deactivation and blocking of active sites. Industrially, these processing techniques are not attractive due to the high mass-transfer resistance and pressure drops they impart.\textsuperscript{189}

Using 3D printing as the manufacturing technique means that these solid-state materials can be processed into structures which impart properties that surpass those if the materials were to have been processed into granular or pelletised forms. 3D printing typically involves the incorporation and dispersion of the active material into a printable paste, ink or filament, followed by the layer-by-layer deposition and hardening of this
mixture to achieve the final structure. Of the many types of 3D printing, direct ink writing (DIW) and fused deposition modelling (FDM) will be discussed as they are relevant to the work conducted in this study.

### 1.5.1 Direct Ink Writing

DIW is an extrusion-based printing technique employing viscoelastic materials such as polymer liquids and hydrogels as the ink to fabricate 3D structures. As shown in Figure 1.18, pneumatic or mechanical pistons apply pressure to a contained vessel containing the shear-thinning ink which may pass through an Archimedes screw and is then extruded through a nozzle in a layer-by-layer process to produce the final structure.

![Figure 1.18: Direct ink writing with an Archimedes screw and mechanical piston.](image)

The most important aspect of controlling the DIW process is the ink’s rheology. The shear stresses arising from the flow of a Newtonian fluid are directly proportional to the shear rate. This means that the viscosity of the fluid does not vary with shear rate, as illustrated in Figure 1.19. This is generally true for low viscosity fluids, which are therefore more suitable for inkjet printing. However, for non-Newtonian fluids, such as the inks used for DIW, the initial viscosity of the ink is high. With the application of a shear rate, the viscosity reduces (shear thinning). This allows for a printable, viscous ink which, once printed, can retain its shape after exiting the nozzle without the need for curing to occur between steps.
1.5.2 Fused Deposition Modelling

FDM is another extrusion-based 3D printing technique. It heats a thermoplastic filament above its glass transition temperature so that the material can flow out of the nozzle. It is deposited layer-by-layer onto a heated substrate, allowing for layers to fuse, yielding the 3D structure.\[190\] This technique, because of the rapid hardening of the printed material, means that complex structures which utilise overhangs are achievable. FDM printers are shown in Figure \[1.20\]

The layer thickness, width, orientation and air gap size between the printed filaments (rasters) are the main processing parameters affecting the properties of the printed parts. Thicker rasters produce mechanically-sound printed part, but cause longer printing time (depending on nozzle size) and uses more material\[191\]
1.5.3 3D Printing Conjugated Polymers

Conjugated polymers (CPs) are generally insoluble in organic solvents, rendering them non-solution-processable. They also have high melting points, and often decompose before they melt. Lowering melting temperatures has been explored in the past by altering the chemical structure of the polymers but this often results in poor electronic performance.\textsuperscript{192}

As a result, the direct printing of CPs is impossible without the loss of electronic properties (FDM) or simply through process-incompatibility (DIW). Therefore, the physical blending of CPs with binders or into low melting point thermoplastics or solution-processable support networks is necessary for the printing of these structures. Whilst there is research going into the melt-processing of CPs, which opens up the feasibility of printing CPs directly using FDM,\textsuperscript{192,193} this research is still in its infancy.

Printing of CPs using DIW is more researched. Mixing PANI EB with dodecylbenzenesulfonic acid (DBSA) at certain ratios allows the DBSA to act as both a dopant to yield the conducting ES and also a binder, creating a viscous paste which can be printed by DIW into complex, conducting structures.\textsuperscript{194} Furthermore, strong $\pi-\pi$ interactions can be formed between reduced graphene oxide and PANI pastes, creating a robust gel network for the application of supercapacitors.\textsuperscript{195}

Using a binder or support network to print porous materials, however, has been seen
to reduce porosity and block catalyst active sites, reducing activity of CMPs for \( \text{ECO}_2 \text{R} \), for example. Despite this, AM is a promising technique for the fabrication of electrodes. Current methods for testing electrocatalysts for \( \text{ECO}_2 \text{R} \) involve drop casting a dispersion of the active material and a binder onto a support, such as glassy carbon electrodes or carbon paper. This means that the amount of catalyst present in tests is difficult to control.

3D printing allows for fine control over electrode design. Passivation of an electrode surface occurs easily if the reaction involves the formation of gaseous products, as is the case for \( \text{ECO}_2 \text{R} \), leading to results which suggest poor catalyst activity when in actuality, trapped bubbles, and therefore blocked active sites, arise from poor electrode design. For example, cylindrical glassy carbon electrodes encased in an outer cylinder of PTFE can easily trap gas on the small electroactive area exposed. It has been shown that electrode geometry impacts the OER, with hole-containing structures preventing bubble detachment and further reaction.

Electrode design can also be used to combat the previous issue highlighted in which porosity and active sites are blocked through blending conjugated polymers with a support system. In some cases, the binders and support networks used do not impair the porosity of porous materials with respect to their weight in the system. However, in some instances, post-modification of printed structures containing porous materials is required due to the blocking of porosity. This has been remedied in FDM through the use of two thermoplastics and a porous material in the filament. Once printed, the structure is exposed to a solvent which one of the two thermoplastics is soluble in, exposing the porous material and allowing for tunable porosity.

Finally, as previously highlighted in Section 1.4.2, vapour-fed electrochemical reactors such as GDEs are to be used for the industrialisation of \( \text{ECO}_2 \text{R} \). However, it is highly important to prevent flooding of the cathode chamber to maintain the gas-solid-liquid interface which prevents \( \text{ECO}_2 \text{R} \) from becoming mass-transport limited. A 3D-printed cathode layer, or even an entirely additive-manufactured GDE, will ensure the tight geometric constraints imposed on the system are satisfied to better the process.
1.6 Summary

The implications of rising atmospheric CO$_2$ levels has been discussed. Of the many CCUS technologies available, ECO$_2$R is one of the most promising, having already reached pilot-scale testing. Its ability to permanently sequester CO$_2$ whilst generating fuels and chemical feedstock will expand a low-carbon economy and close the carbon cycle. There are many catalysts which show promise for this application such as metals, doped carbonaceous materials and MOFs, but high cost and material instability mean that CMPs emerge as a potential candidate for the carbon separation and capture and ECO$_2$R steps in this CCU technique.

PTPA is an N-rich CMP. Favourable interactions between the N and H atoms in PTPA and CO$_2$ molecules and its permanently microporous skeleton means that its CO$_2$ adsorption capacity is high. Its $\pi$-conjugated structure imparts semiconducting properties, also making it a suitable electrocatalyst for ECO$_2$R. Previous work in the Faul research group by Dr Veronica Del Angel Hernandez has shown PTPA to reduce CO$_2$, and the product selectivity to depend on pore size. Due to its insolubility in organic solvents, these tests have been limited to binding PTPA to glassy carbon electrodes (aqueous phase reactors) and carbon cloth (vapour phase reactors). Therefore, in a step to improve the process-ability of PTPA, this project aims to blend this CMP with polymer support networks which are processable, allowing for a material which can be handled.

Blending, however, presents the issue of blocking porosity and active sites, impairing the ability of PTPA to reduce CO$_2$. Here, electrode architecture serves as an important design consideration to minimise these effects by maximising the PTPA exposed to CO$_2$ and enhancing electron transfer during ECO$_2$R. Intricate electrode design can be realised through 3D printing in a step to industrialising PTPA for CO$_2$ capture and reduction.
Aims and Objectives

The overall aim of this project is to formulate 3D-printable inks/filaments by blending polytriphenylamine, a conjugated microporous polymer previously shown by Dr Veronica Del Angel Hernandez to capture and convert CO$_2$, with polymer support networks (PSNs) to print electrodes for electrochemical CO$_2$ reduction. This was achieved by following the 3 objectives:

1. Identify suitable PSNs, considering properties for both processing and application.

2. Test suitability of the composites for electrochemical CO$_2$ reduction.

3. Optimise printing parameters for the printing of high-surface area composite electrodes.
Experimental

3.1 Materials and Methods

Reagents were purchased from Sigma-Aldrich UK and were used as received unless otherwise stated.

A PerkinElmer Spectrum 100 spectrometer was used to acquire the FTIR spectra in the region between 4000 and 400 cm\(^{-1}\).

A Quantachrome Quadrasorb instrument was used for N\(_2\) sorption isotherms and CO\(_2\) adsorption studies, using a static volumetric method. Samples were dried on the Schlenk line at 110°C and then degassed under high vacuum at various degassing profiles, depending on the composite composition as seen in Table 3.1.

Table 3.1: Degassing profiles for polytriphenylamine (PTPA) and composites.

<table>
<thead>
<tr>
<th>Material</th>
<th>Degassing Profile</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTPA</td>
<td>150°C for 5 hours</td>
</tr>
<tr>
<td>Polypropylene-based composites</td>
<td>120°C for 8 hours</td>
</tr>
<tr>
<td>PIM-based composites</td>
<td>180°C for 4 hours</td>
</tr>
</tbody>
</table>

The specific surface areas were calculated from the Brunauer–Emmett–Teller (BET) model using the adsorption branches of the N\(_2\) isotherms in the low pressure range from P/P\(_0\) = 0.05 to P/P\(_0\) = 0.30 at 77.4 K using the QuadraWin 5.05 software package. The pore size distribution was calculated from the desorption branch of the N2 isotherms using nonlocal density functional theory (NL-DFT); Barret, Joyner and Halenda (BJH) and Grand canonical Monte Carlo (GCMC) methodologies were performed using the QuadraWin 5.05 package. CO\(_2\) uptakes (wt%) and CO\(_2\) heats of adsorption values were calculated from CO\(_2\) adsorption isotherms collected at 273 and 298K. Detailed information on the mode of measurement and BET Theory can be found in the Introduction in Subection 1.2.2.

Solid-state UV/Vis-NIR spectra were recorded on a Shimadzu UV-2600 Spectrometer using barium sulphate as the background.
Scanning electron microscopy (SEM) and backscattered electron (BSE) images were recorded using a JEOL 6330 FEG SEM. Samples were either prepared on glass slides which were adhered to the aluminium sample holders using adhesive carbon pads or were directly prepared on the sample holders themselves. All PP samples were sputter-coated with a 15 nm layer of silver.

$^1$H NMR experiments were performed using either a 400 MHz Bruker Nano400 or a 500 MHz Bruker Cryo 500 for proton suppression experiments, and were referenced to deuterated solvents.

Thermal gravimetric analysis experiments were performed using a TGA Q500 and a platinum sample holder. $N_2$ gas was passed over the samples during analysis and a heating rate of $10^\circ C/min$ was used, heating the samples to a maximum of $800^\circ C$. Samples were dried on a Schlenk line at $120^\circ$ for 24 hours before analysis.

Electrochemical CO$_2$ reduction tests were conducted on a Basi C-3 cell stand and the reaction was controlled and measured using a Basi EC Epsilon potentionstat. The 3-electrode cell consisted of a 0.1 M KHCO$_3$ electrolyte, a silver chloride in saturated KCl (Ag/AgCl) reference electrode, Pt counter electrode and PTPA-containing working electrode.

Conductance was measured using a Keithley 2400 SourceMeter connected to 4 probes with a spacing of 3.3 mm. Samples were processed into a wire or kept square or circular to simplify geometric corrections associated with analysis.

Filaments for fused deposition modelling (FDM) were made by melt-mixing the composite in a Hakke Minilab II at 60 revolutions per minute (rpm) and $190^\circ C$. A FilaFab was then used at $190^\circ C$ to extrude the composite into a filament which can then be used for FDM. FDM was conducted on a Creality 3D Ender 3 Pro 3D printer. Direct ink writing (DIW) was conducted on a custom-built printer.
3.2 Polytriphenylamine Synthesis

3.2.1 Regular Polytriphenylamine Synthesis

A Schlenk tube was charged with tris(4-bromophenyl)amine (0.5 mmol, 241 mg), phenylenediamine (0.33 mmol, 35.7 mg to obtain a ratio of core to linker of 1.5:1), Pd(dba)2 (dba = dibenzylideneacetone, 0.03 mmol, 17.3 mg 4 mol%), 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos, 0.045 mmol, 21.5 mg, 9 mol%), sodium tert-butoxide (NaOtBu, 3.5 mmol, 336.35 mg) and sodium fluoride (NaF, 0.5 mmol, 21 mg) and placed under a nitrogen atmosphere. Anhydrous THF (30 mL) was added and the reaction mixture was heated under stirring at 65°C. The Schlenk tube was left open to nitrogen and after 48 hours, was cooled to room temperature. The products were then washed with CHCl₃, ethanol, methanol and boiling water (200 mL each) to remove catalyst, salt and oligomers. A 72 hour Soxhlet extraction followed with methanol, THF and chloroform, respectively, 24 hours each.

3.2.2 Scaled-Up Polytriphenylamine Synthesis

A Schlenk tube was charged with tris(4-bromophenyl)amine (2.5 mmol, 1205 mg), phenylenediamine (1.67 mmol, 178.5 mg to obtain a ratio of core to linker of 1.5:1), Pd(dba)2 (dba = dibenzylideneacetone, 0.15 mmol, 86.5 mg 4 mol%), 2-Dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos, 0.225 mmol, 107.5 mg, 9 mol%), sodium tert-butoxide (NaOtBu, 17.5 mmol, 1682.5 mg) and sodium fluoride (NaF, 2.5 mmol, 105 mg) and placed under a nitrogen atmosphere. Anhydrous tetrahydrofuran (THF) (105 mL) was added and the reaction mixture was heated under stirring at 65°C. The Schlenk tube was left open to nitrogen and after 48 hours, was cooled to room temperature. The products were then washed with CHCl₃, ethanol, methanol and boiling water (200 mL each) to remove catalyst, salt and oligomers. A 72 hour Soxhlet extraction followed with methanol, THF and chloroform, respectively, 24 hours each.
3.3 Composite Formulation

3.3.1 PEO-based Matrices

PEO/PVA/SUPTPA Glutaraldehyde Gels

A 1 wt% glutaraldehyde (GA) solution was prepared by adding 98 mL DI water to 2 mL 50 wt% GA solution. 0.5 mL of this 1 wt% stock solution was added to 4.5 mL water, creating a 0.1 wt% GA solution. The 0.1 wt% GA solution was used to dissolve PVA or PVA/PEO mixtures. PVA or PVA/PEO mixtures were also dissolved in 0.1 M HCl.

These mixtures were prepared inside of plastic luer-lock syringes which could be connected by a 2-way stop cock. To ensure complete dissolution, the syringes were placed inside of a water bath at 80°C and were regularly mixed using an empty syringe and a 2-way stop cock over a period of 2 hours. Following this, the syringes were removed from the water bath and left overnight.

Various amounts of scaled up PTPA (SUPTPA) were added to the acid/polymer mixture, and dispersed using an empty syringe and the 2-way stop cock. The acid/polymer/SUPTPA mixture was then connected to the syringe containing the crosslinker/polymer and mixed quickly and vigorously before casting the mixture into a petri dish. The cast was left to gelate for an hour, before removing from the petri dish and washing thoroughly with water, then adding to 0.1 M NaOH to neutralise, then washing thoroughly once again with water until the pH of the solution the gel was placed in was neutralised.

The amounts of reactants are shown in Table 3.2. All PVA or PVA/PEO solutions concentrations were 10 w/v% (weight of polymer/weight of solution). The amounts of SUPTPA added were such that it contributed 10% to the overall weight (10 w/w%) of the polymers in the composite. Before addition, SUPTPA was ground to a fine powder. The colours on Table 3.2 indicate which inks (numbered) were mixed to create which composite (letter). For example, ink 1 and 2 were mixed to create composite A.
Table 3.2: Amounts of reagents used in GA-based gel formulation.

<table>
<thead>
<tr>
<th>Ink</th>
<th>0.1 wt% GA Solution (mL)</th>
<th>0.1M HCl (mL)</th>
<th>PVA (mg)</th>
<th>PEO (mg)</th>
<th>SUPTPA (mg)</th>
<th>Gel</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>-</td>
<td>500</td>
<td>-</td>
<td>-</td>
<td>A</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>5</td>
<td>500</td>
<td>-</td>
<td>-</td>
<td>A</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>-</td>
<td>400</td>
<td>100</td>
<td>-</td>
<td>B</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
<td>5</td>
<td>400</td>
<td>100</td>
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<td>B</td>
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<tr>
<td>5</td>
<td>5</td>
<td>-</td>
<td>500</td>
<td>-</td>
<td>55.56</td>
<td>C</td>
</tr>
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<td>5</td>
<td>500</td>
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<td>-</td>
<td>C</td>
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<td>100</td>
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<td>-</td>
<td>5</td>
<td>400</td>
<td>100</td>
<td>-</td>
<td>D</td>
</tr>
</tbody>
</table>

PEO/PVA/SUPTPA Terephthalaldehyde Gels

A 0.1 wt% terephthaldehyde (TPA) solution was prepared by adding 100 mg TPA to 100 mL water, which was then heated to 80°C with stirring until complete dissolution. The 0.1 wt% TPA solution was used to dissolve PVA or PVA/PEO mixtures. PVA or PVA/PEO mixtures were also dissolved in 0.1 M HCl. These mixtures were prepared inside of plastic luer-lock syringes which could be connected by a 2-way stop cock. To ensure complete dissolution, the syringes were placed inside of a water bath at 80°C and were regularly mixed using an empty syringe and a 2-way stop cock over a period of 2 hours. Following this, the syringes were removed from the water bath and left overnight.

Various amounts of SUPTPA were added to the acid/polymer mixture, and dispersed through the use of an empty syringe and the 2-way stop cock. The acid/polymer/SUPTPA mixture was then connected to the syringe containing the crosslinker/polymer and mixed quickly and vigorously before casting the mixture into a petri dish. The cast was left to gelate for an hour, before removing from the petri dish and washing thoroughly with water, then adding to 0.1 M NaOH to neutralise, then washing thoroughly once again with water until the pH of the solution the gel was placed in was neutralised.

The amounts of reactants are shown in Table 3.2. All PVA or PVA/PEO solutions were 10 w/v% (weight of polymer/weight of solution). The amounts of SUPTPA added were such that it contributes 10 w/w% to the overall weight of polymers in the composite. Before addition, SUPTPA was ground to a fine powder. The colours in Table 3.2 indicate
which inks (numbered) were mixed to create which composite (letter). For example, ink 9 and 10 were mixed to create composite E.

Table 3.3: Amounts of reagents used in TPA-based gel formulation.

<table>
<thead>
<tr>
<th>Ink</th>
<th>0.1 wt% TPA Solution (mL)</th>
<th>0.1M HCl (mL)</th>
<th>PVA (mg)</th>
<th>PEO (mg)</th>
<th>SUPTPA (mg)</th>
<th>Gel</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>5</td>
<td>-</td>
<td>500</td>
<td>-</td>
<td>-</td>
<td>E</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>5</td>
<td>500</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>5</td>
<td>-</td>
<td>400</td>
<td>100</td>
<td>-</td>
<td>F</td>
</tr>
<tr>
<td>12</td>
<td>-</td>
<td>5</td>
<td>400</td>
<td>100</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>5</td>
<td>-</td>
<td>500</td>
<td>-</td>
<td>55.56</td>
<td>G</td>
</tr>
<tr>
<td>14</td>
<td>-</td>
<td>5</td>
<td>500</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>5</td>
<td>-</td>
<td>400</td>
<td>100</td>
<td>55.56</td>
<td>H</td>
</tr>
<tr>
<td>16</td>
<td>-</td>
<td>5</td>
<td>400</td>
<td>100</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

PEGDA/SUPTPA Composites

Polyethylene glycol diacrylate (PEGDA) and photoinitiator 2-hydroxy-4’-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959) were dissolved in deionised (DI) water. Irgacure 2959 was added such that 0.1, 0.2 and 0.3 w/w% (weight of photoinitiator/weight of PEGDA and photoinitiator) was tested. This solution was sonicated for 1 hour to obtain a homogenised, bubble-free solution before drop casting into a film. The film was exposed to UV light in a reactor for 30s (the distance of the light guide to the guide to the film was optimised to 200mWcm⁻²), causing free radical photopolymerisation to form a cross-linked PEGDA/Irgacure 2959 network. The amounts used are in Table 3.4.

The optimal composition in terms of structural integrity was selected. The composite was formulated with the addition of SUPTPA into the initial composition. SUPTPA was ground to a fine powder, and added such that it contributed 10 w/w% of the polymers in the composite (weight of PTPA/weight of PTPA, PEGDA and photoinitiator). To ensure good dispersion of SUPTPA, the mixture was sonicated for 2 hours before being cast into a film and exposed to ultraviolet light in a UV reactor for 30s.
Table 3.4: Amounts of reactants used to formulate PEGDA composites.

<table>
<thead>
<tr>
<th>PEGDA (mL)</th>
<th>Water (mL)</th>
<th>Irgacure 2959 (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15.0</td>
</tr>
<tr>
<td>4.5</td>
<td>0.5</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13.5</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.0</td>
</tr>
<tr>
<td>3.5</td>
<td>1.5</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.5</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.0</td>
</tr>
</tbody>
</table>

3.3.2 Polypropylene

Polypropylene/CB/GN/SUPTPA Composite Solution Mixing

Ground SUPTPA and/or carbon black (CB) and/or graphene nanoplatelets (GN) was dispersed in 10 mL xylene in a round bottom flask (RBF) and stirred for 2 hours using a magnetic stirrer. 150 mg of low $M_w$ polypropylene (PP) and 150 mg of high $M_w$ PP was added and a reflux condenser was fitted to the RBF with cold water running.

The RBF was heated to 130°C under strong stirring and left for 2 hours to ensure complete dissolution of the PP before removing from the heat and allowing to cool. The contents of the RBF was poured into a large beaker containing 200 mL ethanol to precipitate the composite. The RBF was sprayed with ethanol to precipitate any remaining composite. The product was collected then vacuum filtered for 15 minutes to remove excess solvent before drying on a Schlenk line. The amounts used are in Table 3.5.

The names of the composites are in the format PP-SUPTPA$X$CB$Y$GN$Z$ where $X$, $Y$, and $Z$ represent the amount of SUPTPA, CB, and GN used, respectively, in milligrams.
Y and Z represent the w/w% each component contributes to the overall weight of the composite. For example, the composite PP-CB15SUPTPA15 consists of 15%w/w CB, 15%w/w SUPTPA, 35%w/w low M$_{w}$ PP and 35%w/w high M$_{w}$ PP.

Table 3.5: Amounts used in PP composite formulation.

<table>
<thead>
<tr>
<th>Composite</th>
<th>SUPTPA (mg)</th>
<th>CB (mg)</th>
<th>GN (mg)</th>
<th>Low M$_{w}$ PP (mg)</th>
<th>High M$_{w}$ PP (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-SUPTPA10</td>
<td>33.3</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PP-SUPTPA20</td>
<td>75.0</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PP-SUPTPA30</td>
<td>128.6</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PP-CB15</td>
<td>-</td>
<td>52.9</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PP-CB15SUPTPA15</td>
<td>64.3</td>
<td>64.3</td>
<td>-</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>PP-GN15</td>
<td>-</td>
<td>-</td>
<td>52.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PP-GN15SUPTPA15</td>
<td>64.3</td>
<td>-</td>
<td>64.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PP-CB7.5GN7.5</td>
<td>-</td>
<td>26.5</td>
<td>26.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PP-CB7.5GN7.5-SUPTPA15</td>
<td>64.3</td>
<td>32.1</td>
<td>32.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Once dried, the composites were shaped into wires using a brass mould. The mould was clamped to a hot plate and the temperature was set to 185°C. The composite was pressed into the mould using a wide spatula and once filled, the mould was removed from the heat. Once sufficiently cool, the wire was removed from the mould using a needle.

Polypropylene/CB/SUPTPA Filament Formulation

1 g SUPTPA and 1 g CB was dispersed in 100 mL xylene in a RBF and stirred for 2 hours using a magnetic stirrer. After this time, 2.333 g of low Mw PP and 2.333 g of high Mw PP was added and a reflux condenser was fitted to the RBF with cold water running.

The RBF was heated to 130°C under strong stirring and left for 2 hours to ensure complete dissolution of the PP before removing from the heat and allowing to cool for 5 minutes. The contents of the RBF was poured into a large beaker containing 800 mL ethanol to precipitate the composite. The inside of the RBF was also sprayed with ethanol to precipitate any remaining composite on the walls. The product was collected
then vacuum filtered for 15 minutes to remove excess solvent before drying on a Schlenk line.

The composite was then melt-mixed and extruded to formulate a long filament for printing via fused deposition modelling (FDM).

**Fused Deposition Modelling**

Autodesk Inventor was used to model different electrode designs which were exported under a stereolithography (STL) file format. A base to the electrodes were added in the design, to be printed with pure polypropylene, to improve structural integrity and provide a means of establishing an electrical connection with the electrode and the potentiostat. To ensure the printing of a high-quality and mechanically-sound electrode, the thickness of the electrode walls had to be a minimum of two multiples of the printer nozzle diameter.

The STL file was loaded in Octoprint, a slicer software, and the following parameters (which had been optimised for polypropylene filaments with high contents of porous carbons by PhD student Sam Deeks) for FDM were defined at this step. The parameters in Table 3.6 were saved under a g-code file which could be loaded in Octoprint to enable the printing of electrodes in a layer-by-layer fashion.

Spools of filament were attached to the printer heads, with one head printing pure polypropylene (for the electrode base) and the other for the SUPTPA-containing filament. It was necessary to extrude a small amount of material through both printer heads before electrode printing began to ensure a high-quality electrode print. The bed was heated to ensure good adhesion between layers and adhesion of the electrode base to the bed. The bed was covered with tape, improving adhesion and allowing for an easy way to remove the electrode once printing was complete.
Table 3.6: FDM printing parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed temperature</td>
<td>80°C</td>
</tr>
<tr>
<td>Extruder temperature</td>
<td>180°C</td>
</tr>
<tr>
<td>Extruder diameter</td>
<td>0.35 mm</td>
</tr>
<tr>
<td>Extrusion multiplier</td>
<td>0.93</td>
</tr>
<tr>
<td>Retraction distance</td>
<td>0.5 mm</td>
</tr>
<tr>
<td>Retraction speed</td>
<td>6000 mm/min</td>
</tr>
<tr>
<td>First layer height</td>
<td>70%</td>
</tr>
<tr>
<td>Internal fill pattern</td>
<td>Rectilinear</td>
</tr>
<tr>
<td>External fill pattern</td>
<td>Rectilinear</td>
</tr>
<tr>
<td>Print speed</td>
<td>3600 mm/min</td>
</tr>
<tr>
<td>Outline underspeed</td>
<td>60%</td>
</tr>
<tr>
<td>Solid infill underspeed</td>
<td>80%</td>
</tr>
<tr>
<td>Infill Percentage</td>
<td>85%</td>
</tr>
<tr>
<td>Coasting distance</td>
<td>0.08 mm</td>
</tr>
<tr>
<td>Extruder wipe distance</td>
<td>0.25 mm</td>
</tr>
<tr>
<td>Max. overhang angle</td>
<td>60°</td>
</tr>
</tbody>
</table>

### 3.3.3 Polymers of Intrinsic Microporosity (PIMs)

**PIM-1 Synthesis**

A Schlenk tube was charged with 3,3,3′,3′-tetramethyl-1,1′-spirobiindane-5,5′,6,6′-tetraol (5.11 g, 14.6 mmol) and tetrafluoroterephthalonitrile (3.0 g, 14.7 mmol, previously purified by recrystallization from hot acetone). The reagents were stirred under a \( \text{N}_2 \) atmosphere in 100 mL anhydrous dimethylformamide (DMF) and the heat was set to 65°C. Once up to temperature, anhydrous potassium carbonate (\( \text{K}_2\text{CO}_3 \) 16.59 g, 120 mmol), which was previously ground to a fine powder and left under vacuum overnight, was added. The reaction was left for 72 hours under nitrogen at 65°C. On cooling, the suspension was poured into water (300 mL) and the yellow powder was separated by filtration before washing with excessive amounts of water followed by acetone. The powder was left to dry under vacuum before half was collected, dissolved in 100 mL chloroform.
and reprecipitated in methanol (900 mL). Reprecipitation was repeated 3 times and for both halves of reaction product separately. The product was collected as bright yellow granules that were dried under vacuum at 80°C.

**PIM-1/SUPTPA/CB Composite Formulation**

PIM-1, CB and SUPTPA were added to THF (about 40 mg PIM-1 per mL THF) and left in a high-powered tip sonicator for 30 minutes to break up CB aggregates. The solution was then left shaking overnight to ensure complete dissolution of PIM-1 before being cast into a petri dish. The petri dish was immediately covered and the solvent left to slowly evaporate over the course of 2 days.

Table 3.7: Amounts used in PIM-1 composite formulation.

<table>
<thead>
<tr>
<th>Composite</th>
<th>SUPTPA (mg)</th>
<th>CB (mg)</th>
<th>PIM-1 (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIM1</td>
<td>-</td>
<td>-</td>
<td>200</td>
</tr>
<tr>
<td>PIM1-SUPTPA5</td>
<td>10.5</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>PIM1-SUPTPA10</td>
<td>22.2</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>PIM1-SUPTPA20</td>
<td>50</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>PIM1-CB5SUPTPA15</td>
<td>37.5</td>
<td>12.5</td>
<td></td>
</tr>
<tr>
<td>PIM1-CB10SUPTPA10</td>
<td>25</td>
<td>25</td>
<td></td>
</tr>
</tbody>
</table>

The film was removed from the petri dish (the use of a few drops of water helped to remove the film if stuck) and dried on a Schlenk line at 120°C. The amounts used in the composites are shown in Table 3.7. The names used have the same nomenclature as in Table 3.5, where numbers indicate the percentage by which each component contributes to the overall weight of the composite.

**PIM-1 Ink Formulation**

PIM-1, DMAc and THF in varying amounts were added to a glass PTFE luer lock Hamilton 1000 series 10 mL syringe (Model 1010 TLL) and sealed shut. The syringe was left in a 50°C oven and over the course of 48 hours, was periodically mixed using a vortex mixer. The use of dimethylacetamide (DMAc) increases the boiling point of the solvent for the purpose of direct ink writing (DIW). The quantities used in the inks are shown in Table 3.8.

The ink name is in the format of $\text{PIM1}^\alpha/\text{THF}^\beta/\text{DMAc}^\gamma$ where $\alpha$, $\beta$ and $\gamma$ represent...
the weight for weight percentage each component contributes to the overall weight of the ink. For example, ink PIM10.2/THF0.46/DMAc0.34 consists of 20%w/w PIM-1, 46%w/w THF and 34%w/w DMAc. The densities of the solvents are used to convert the weight to mL.

Table 3.8: Amounts used in PIM-1 ink formulation.

<table>
<thead>
<tr>
<th>Ink</th>
<th>PIM-1 (mg)</th>
<th>THF (mL)</th>
<th>DMAc (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I  PIM0.2/THF0.46/DMAc0.34</td>
<td>700</td>
<td>1.81</td>
<td>1.27</td>
</tr>
<tr>
<td>J  PIM0.22/THF0.41/DMAc0.37</td>
<td>1.47</td>
<td>1.25</td>
<td></td>
</tr>
<tr>
<td>K  PIM0.17/THF0.54/DMAc0.29</td>
<td>2.50</td>
<td></td>
<td>1.27</td>
</tr>
</tbody>
</table>

**PIM-1/SUPTPA/CB Ink Formulation**

SUPTPA and CB was incorporated into the ink composition which showed the greatest printability. PIM-1, SUPTPA and CB were added to an excess of THF and left in a high powered sonicator for 1 hour to break up CB aggregates. The THF was then allowed to evaporate so that a composite consisting of PIM-1, SUPTPA and CB remained (slow evaporation at this stage was not necessary). This composite was dried under vacuum overnight at 80°C.

The composite was then crushed and added to a glass PTFE luer lock Hamilton 1000 series 10 mL syringe (Model 1010 TLL) and sealed shut. The syringe was left in a 50°C oven and over the course of 48 hours, was periodically mixed using a vortex mixer. The quantities used are shown in Table 3.9. The amounts of solvent used were not influenced by the addition of SUPTPA and CB.

The ink name is in the format of $\delta$-CB$\epsilon$SUPTPA$\mu$, where $\delta$ indicates the ink used in the formulation, as selected from Table 3.8 and $\epsilon$ and $\mu$ represent the weight for weight percentage each solid component contributes to the overall weight of the composite once the solvent has evaporated. For example, composite K-CB10SUPTPA10 uses ink K from Table 3.8 and consists of 80%w/w PIM-1, 10%w/w CB and 10%w/w SUPTPA.
Experimental

Table 3.9: Amounts used in SUPTPA-containing PIM-1 ink.

<table>
<thead>
<tr>
<th>PIM-1 (mg)</th>
<th>THF (mL)</th>
<th>DMAc (mL)</th>
<th>Composite</th>
<th>CB (mg)</th>
<th>SUPTPA (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>2.50</td>
<td>1.27</td>
<td>K-CB10SUPTPA10</td>
<td>87.5</td>
<td>87.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>K-CB5SUPTPA15</td>
<td>43.7</td>
<td>131.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>K-CB5SUPTPA5</td>
<td>38.9</td>
<td>38.9</td>
</tr>
</tbody>
</table>

Direct Ink Writing

Autodesk Inventor was used to model different electrode designs which were exported under a stereolithography (STL) file format. To ensure the printing of a high-quality and mechanically-sound electrode, the thickness of the electrode walls had to be a minimum of two multiples of the printer nozzle diameter.

The STL file was loaded in Simplify 3D, a slicer software, and the following parameters for DIW were defined at this step. The parameters in Table 3.10 were saved under a g-code file, enabling electrode printing in a layer-by-layer fashion.

The ink pathway was flooded with THF before connecting the syringe to the printer; this prevented solvent evaporation and clogging of the channel, enabling a continuous flow of ink. A gas inlet of house N\(_2\) was connected to the syringe, and the N\(_2\) pressure was set to 80 mbar. Paper was attached to the printer bed to be used as the printing substrate, and the distance between the printer nozzle and substrate was modified with every print to ensure a paper-thickness distance. It was necessary to extrude a small amount of material before electrode printing began to ensure a high-quality electrode print.
Table 3.10: DIW printing parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extruder diameter</td>
<td>0.8 mm</td>
</tr>
<tr>
<td>Extrusion multiplier</td>
<td>5</td>
</tr>
<tr>
<td>Retraction distance</td>
<td>0.05 mm</td>
</tr>
<tr>
<td>Retraction speed</td>
<td>5000 mm/min</td>
</tr>
<tr>
<td>First layer height</td>
<td>80%</td>
</tr>
<tr>
<td>Internal fill pattern</td>
<td>Rectilinear</td>
</tr>
<tr>
<td>External fill pattern</td>
<td>Rectilinear</td>
</tr>
<tr>
<td>Outline overlap</td>
<td>50%</td>
</tr>
<tr>
<td>Print speed</td>
<td>400 mm/min</td>
</tr>
<tr>
<td>Outline underspeed</td>
<td>100%</td>
</tr>
<tr>
<td>Solid infill underspeed</td>
<td>80%</td>
</tr>
</tbody>
</table>
3.3.4 Electrochemical CO₂ Reduction Testing

Electrochemical tests were conducted in custom-made H-cells containing 5 cm³ of 0.1 M KHCO₃ electrolyte in each compartment, purged with either CO₂ or Ar for 2 hours prior to use.

![H-cells](image)

(a) Circular H-cell.   (b) Square H-cell.

Figure 3.1: H-cells used for ECO₂R tests.

Before measurements, the electrolyte pH was measured. Between tests, the electrolyte was changed, with the pH recorded with each replenishment. The working, reference and counter electrodes as well as the CO₂ and Ar gas inlets were held using an electrode holder, fitted to the dimensions of the H-cell, printed by FDM, as seen in Figure 3.2.

![Electrode and gas inlet holder](image)

Figure 3.2: Electrode and gas inlet holder.

Cyclic voltammetry (CV) and chronoamperometry (CA) were used to test material suitability for electrochemical CO₂ reduction (ECO₂R). For the materials, the CV ranges investigated were:
-1 to 0 V vs RHE for 2 cycles
-1 to 1 V vs RHE for 32 cycles

CA lasted 30 minutes, and the potentials investigated for the materials were:

-0.2 vs RHE
-0.4 vs RHE
-0.5 vs RHE
-0.7 vs RHE
-0.9 vs RHE
-1.0 vs RHE

After chronoamperometry, the electrolyte on the cathodic side of the cell was collected for product detection with NMR spectroscopy. To determine the amount of product produced, which in turn allows the determination of the Faradaic efficiency of the system, 10 µL of 1 mM maleic acid was added (alongside 180 µL of D₂O and 600 µL of the collected electrolyte) to the NMR tube as an internal standard.

**Polytriphenylamine**

A glassy carbon electrode (GCE), purchased from BASi Research products, with a GC diameter of 7 mm, was used to test SUPTPA for ECO₂R. A microcloth was adhered to a glass polishing pad. The electrode surface was rinsed with DI water, followed by methanol, before being wiped with a fresh tissue. The polishing cloth was wetted with DI water and a suspension containing 0.05µm alumina particles was shaken before several drops of the suspension were spaced evenly over the microcloth surface.

The GCE was placed face-down and, applying an even pressure whilst using a circular motion, the electrode was polished in a figure-of-eight motion. The direction and rotation of this motion was changed regularly to ensure even wear of the electrode. After 2 minutes of polishing, the electrode surface was rinsed with DI water and then submerged in a shallow amount of distilled water and the sonicated for 3 minutes to remove residual abrasive particles.
SUPTPA was ground to a fine powder and 2 mg was added to a vial, followed by 1 mL of 2-propanol. This mixture was sonicated for 1 hour to obtain a dispersion of SUPTPA in 2-propanol. 20 µL of Nafion perfluorinated resin solution (5 w% Nafion in a mixture of lower aliphatic alcohols and water) was added and the solution was sonicated for a further 5 minutes.

40 µL of this suspension was drop cast onto the GCE surface. The GCE was left drying in a room temperature vacuum oven to obtain a SUPTPA-covered GCE for ECO₂R testing.

**Polypropylene Composites**

Electrical connections were established with the polypropylene wires, formed as described in Subsection 3.3.2 through the use of crocodile clips. The wire used was long enough to ensure that the crocodile clip was not splashed during cell operation to prevent signal noise.

Printed polypropylene electrodes had a pure-polypropylene base containing 0.5 mm holes. Silver wires were soldered to the polypropylene electrode. Once attached, the silver wire was fed through an electrode holder (printed by FDM, shown in Figure 3.3). A crocodile clip was attached to the silver wire as a means of establishing an electrical connection. To ensure good coverage of the PP electrode by the electrolyte, 10 cm³ of 0.1 M KHCO₃ was used in this instance.
PIM-1 Composites

PIM-1 composite films were cast onto glass slides and removed once evaporation was complete to obtain a film long enough to hold by a crocodile clip without it getting splashed during cell operation. Printed PIM-1 composite electrodes were long rectangular shapes which were again held by a crocodile clip at a sufficient distance away from the electrolyte to prevent signal noise.
Results and Discussion

4.1 Polytriphenylamine

4.1.1 Synthesis

Buchwald-Hartwig cross-coupling (BHCC) was used for the synthesis of polytriphenylamine (PTPA), a N-rich conjugated microporous polymer (CMP). The reaction scheme is shown below.

The reaction mechanism follows that described in Section 1.3.1 in Figure 1.10. The Pd catalyst, \( \text{Pd(dba)}_2 \), forms a complex with the ligand, XPhos. The Pd inserts itself into tris(4-bromophenyl)amine (core) and subsequently p-phenylenediamine (linker) co-ordinates with Pd via ligand exchange. The strong base sodium tert-butoxide (\( \text{NaO}t\text{Bu} \)) removes the Br to form NaBr and in the final step, reductive elimination regenerates the Pd-XPhos complex whilst producing C-N bonds.

The synthesis followed to formulate PTPA was adapted from Chen et al., with reagent amounts and techniques discussed in Section 3.2.1. A core to linker ratio of 1.5:1 was used to obtain a high-surface-area CMP. Yields were on the scale of 100 mg (percentage yields are shown in Table 4.1). PTPA is shown in the Figure 4.2.
Results and Discussion

With the objective to blend PTPA with polymer support networks (PSNs), it became quickly apparent that scaling up the synthesis was necessary. To do this, reagent quantities were multiplied by 5 (amounts are shown in Subection 3.2.2) to produce scaled-up PTPA (SUPTPA) on the scale of approximately 800 mg. Yields are shown below in Table 4.1.

Table 4.1: Yields of PTPA and reaction conditions (core = tris(4-bromophenyl)amine, linker = phenylenediamine. Reactions were heated to 65°C and were left stirring under N₂ for 48 hours.

<table>
<thead>
<tr>
<th>Type</th>
<th>Core (mg)</th>
<th>Linker (mg)</th>
<th>NaOtBu (mg)</th>
<th>NaF (mg)</th>
<th>XPhos (mg)</th>
<th>Pd(dba)₂ (mg)</th>
<th>THF (mL)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTPA</td>
<td>241</td>
<td>35.7</td>
<td>336.35</td>
<td>21</td>
<td>21.5</td>
<td>17.3</td>
<td>50</td>
<td>99.7</td>
</tr>
<tr>
<td>SUPTPA</td>
<td>1205</td>
<td>178.5</td>
<td>1682.5</td>
<td>105</td>
<td>107.5</td>
<td>86.5</td>
<td>150</td>
<td>20.7</td>
</tr>
<tr>
<td>SUPTPA</td>
<td>1205</td>
<td>178.5</td>
<td>1682.5</td>
<td>105</td>
<td>107.5</td>
<td>86.5</td>
<td>100</td>
<td>93.2</td>
</tr>
</tbody>
</table>

As can be seen from Table 4.1, initial SUPTPA yields were low, resulting from the larger reaction vessel which in turn decreased the likelihood of reagents interacting and reactions occurring. To counteract these effects, the solvent content was lowered, reducing the reaction volume.

The 48-hour reaction time highlighted in Section 3.2.1 ensured complete reaction of all reagents and a highly cross-linked, microporous network. Whilst the visual appearance of SUPTPA was identical to that of PTPA (Figure 4.2), to confirm that physical properties were not affected through the synthesis of SUPTPA in a lower solvent quantity, characterisation techniques were used to both characterise and compare PTPA and SUPTPA.
4.1.2 Characterisation

Fourier Transform Infrared Spectroscopy (FTIR) was used to ascertain whether the reaction ran to completion. Successful reaction would be indicated by the disappearance or strong attenuation of the absorptions corresponding to: aromatic C-Br stretching (1178 cm\(^{-1}\)) arising from tris(4-bromophenylamine) (pink line in Figure 4.3) and -NH\(_2\) stretching (3420 cm\(^{-1}\)) and deformation (1650 cm\(^{-1}\)) arising from p-phenylenediamine (green lines in Figure 4.3). Both PTPA and SUPTPA show strong attenuation of the aforementioned absorptions.

![Figure 4.3: FTIR spectra of PTPA, SUPTPA and monomers.](image)

Both PTPA and SUPTPA show this attenuation/disappearance for the aforementioned absorptions, indicating reaction between the core and the linker to produce the N-rich network.
Results and Discussion

Figure 4.4 shows the ultra-violet/visible near infra-red (UV-Vis-NIR) spectra of PTPA and SUPTPA. They both exhibit a peaks at approximately 380 nm, which is attributed to the $\pi-\pi^*$ transition of benzenoid ring. The peak attributed to the $\pi-\pi^*$ transition of the quinoid ring is typically measured at 650 nm, however there is clear shifting of the peak arising from the bathochromic effect. The increase in conjugation length, caused by the highly cross-linked structure of PTPA and SUPTPA, decreases the energy difference between the HUMO (occupied by $\pi$ electrons) and the LUMO in the conjugated structure. This decrease in energy difference increases the wavelength of light that is absorbed as a result of this excitation. Therefore, the $\pi-\pi^*$ transition of the quinoid ring is measured at 750 nm.

Thermogravimetric analysis (TGA) was conducted on PTPA and SUPTPA to measure the percentage weight loss as temperature changes over a period of time. This gives information about the physical characteristics of the material being analysed, such as any phase transitions and any physisorption or chemisorption. It indicates the ability of the material to withstand high temperatures.
Figure 4.5: Weight retention rate as a function of temperature for PTPA and SUPTPA (sudden spikes in the graph are a result of benchtop agitation).

Figure 4.5 shows the percentage weight retention as the temperature is increased for PTPA and SUPTPA. There are no sharp transitions, which is expected when components of a material are vaporised. Both PTPA and SUPTPA retain 100% of their weight up to 100°C. They both exhibit a gradual loss of weight up to 800°C at which point 60% of the original weight is retained, which demonstrates the thermal stability of CMPs.

Typical percentage weight loss against temperature curves for CMPs show sudden weight loss at temperatures, indicating the onset of decomposition of the material, rather than the gradual weight loss as depicted in Figure 4.5. There are many reasons for the gradual weight loss seen, such as insufficient drying of the samples (weight loss proceeds after 100°C, the boiling point of water), or the formation of small polymer chains during synthesis, which decompose at lower temperatures than larger chains. Repeats of these measurements are required to confidently ascribe a reason for the gradual weight loss.

SEM images were obtained to confirm and compare the morphology of PTPA and SUPTPA. The images cannot be directly related to the surface area of these materials or their CO₂ uptake capacity but can provide information on the shape of the structure on the nanoscale, as well as the degree of aggregation.
Results and Discussion

(a) PTPA, 500x magnification.

(b) PTPA, 2000x magnification.

(c) SUPTPA, 500x magnification.

(d) SUPTPA, 2000x magnification.

Figure 4.6: SEM images of PTPA and SUPTPA (scale bar at 500x magnification: 50µm, scale bar at 2000x magnification: 10µm

As can be seen in Figure 4.6, both PTPA and SUPTPA possess an amorphous morphology, as is characteristic of CMPs. Their structure consists of distinct nanoparticles which are on the scale of 200-500 nm. The high degree of aggregation these particles exhibit give rise to interstitial voids, contributing to the porosity which was measured using N\textsubscript{2} porosimetry.

Figure 4.7 shows the adsorption/desorption N\textsubscript{2} isotherm for PTPA and SUPTPA (Table 4.2 gives numerical values determined from these graphs). Both isotherms give a combination of the IUPAC isotherm type I and IV. They exhibit a high initial volume of N\textsubscript{2} adsorbed, indicating high degrees of microporosity, and the amount adsorbed continues to increase at high partial pressures, indicating the presence of mesopores and macropores.

The isotherms also exhibit hysteresis throughout the partial pressure range, which is a result of pore condensation. Attractive interactions between the adsorbed molecules in
Results and Discussion

their liquid state causes the difference between the adsorption and desorption points.

The sharp decrease at a partial pressure of approximately 0.43 during desorption which both PTPA and SUPTPA exhibit is commonly seen in hysteresis loops; the closure point of hysteresis is determined by the tensile strength of the capillary-condensed liquid. This means that a mechanical stability limit of condensed N\textsubscript{2} menisci in meso- and macropores exists, after which there is a sudden expulsion of adsorbed N\textsubscript{2}\textsuperscript{50}.

Isotherms revealing type H3 hysteresis do not exhibit any limiting adsorption at high PIPo, which is observed with non-rigid aggregates of plate-like particles giving rise to slit-shaped pores. The desorption branch for type H3 hysteresis contains also a steep region associated with a (forced) closure of the hysteresis loop, due to the so-called tensile strength effect. This phenomenon occurs for nitrogen at 77K in the relative pressure range from 0.4 - 0.45 (see chapter 8.6.2 for a detailed discussion).

Neither isotherm closes perfectly (i.e. the last desorption point sits higher than the first adsorption point) because both materials are retaining some of the N\textsubscript{2}, indicating a degree of chemisorption.

![Figure 4.7: N\textsubscript{2} adsorption/desorption isotherms for PTPA and SUPTPA.](image)

A pore size distribution (PSD) was obtained for both PTPA and SUPTPA to indicate the size of the pores present in both materials and the contribution of these pores to their
overall surface areas. As can be seen in Figure 4.8, PTPA and SUPTPA contain both meso- and macropores, but predominantly small mesopores. The microporosity of PTPA and SUPTPA can be inferred from the high \( \text{N}_2 \) uptakes at low partial pressures in their adsorption-desorption isotherms (i.e. at partial pressures less than 0.05). Repeats of the adsorption measurements where partial pressures below 0.05 are investigated will show the contribution of micropores to the overall PSD (as micropore filling occurs before meso- and macropore filling at low partial pressures). However, to save time these measurements were not made, as probing the microporous region extends measurement times drastically.

Meso- and macropores provide pathways for molecules to reach internal pores, improving gas uptake. In catalysis, this allows charged species and electrolyte access to internal pores and active sites, making SUPTPA suitable for ECO\(_2\)R. This, alongside the favourable interactions between CO\(_2\), amines and aromatic groups (Section 1.2.1) can explain the high CO\(_2\) uptake seen for PTPA and SUPTPA.

PTPA and SUPTPA CO\(_2\) uptake isotherms were measured at 273 and 298K (Figures A.1 and A.2 in the Appendix). Table 4.2 shows the BET surface area and CO\(_2\) uptakes at 273 and 298 K for PTPA and SUPTPA, which show similar values. The CO\(_2\) uptakes exceeds that of other structurally-similar CMPs.\(^\text{[51]}\)
Table 4.2: Porosity and CO\textsubscript{2} uptake for PTPA and SUPTPA.

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface Area (m\textsuperscript{2}/g)</th>
<th>CO\textsubscript{2} uptake at 273 K (wt%)</th>
<th>CO\textsubscript{2} uptake at 298 K (wt%)</th>
<th>CO\textsubscript{2} Q\textsubscript{ST} (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTPA</td>
<td>757.4</td>
<td>12.9</td>
<td>7.7</td>
<td>33.2</td>
</tr>
<tr>
<td>SUPTPA</td>
<td>724.4</td>
<td>12.7</td>
<td>7.6</td>
<td>16.3</td>
</tr>
</tbody>
</table>

Heat of adsorption ($Q_{ST}$) values were determined by using a form of the Clausius Clapeyron equation. Firstly, CO\textsubscript{2} adsorption isotherms at 273 K and 298 K were fitted with the Langmuir model of adsorption to obtain an equation describing the curve. This equation was rearranged to obtain the partial pressure as a function of the fitted equation.

$$\frac{P}{P_0} = \left( \frac{Q_a}{ab - Q_ab} \right)^{1-c} \quad (4.1)$$

$Q_a$ is the amount adsorbed in mmol/g and $a$, $b$ and $c$ are values returned by the fitted equation. The upper and lower limits of $Q_a$ values which were inputted into the equation was the same for both isotherms. The upper limit was dictated by the isotherm of the lowest ultimate $Q_a$ value, whilst the lower limit was dictated by the highest initial quantity adsorbed between the two isotherms. 18 linearly-spaced adsorption data points were selected and put into Equation 4.1 to return $P/P_0$ values for both isotherms. Equation 4.2 was used to determine $Q_{ST}$ values for each partial pressure following this.

$$H_{ads} = R \left( \frac{\delta\ln(P/P_0)}{\delta 1/T} \right) \quad (4.2)$$

$T$ is the isotherm temperature. This plots $\ln(P/P_0)$ against $1/T$ to give straight line graphs. The gradient is $Q_{ST}$ at a certain partial pressure.
Results and Discussion

Figure 4.9: $\ln(P/P_0)$ against $1/T$ plots.

The gradient is $Q_{ST}$ at a certain partial pressure of the lines in Figure 4.9. $Q_{ST}$ was then plotted against the amount adsorbed.
Results and Discussion

Figure 4.10: $Q_{ST}$ plots.

The heat of adsorption is obtained by taking $Q_{ST}$ for the lowest amount adsorbed. 33.2 and 16.3 kJ/mol indicate that interactions of PTPA and SUPTPA and CO$_2$ occur by physisorption (chemisorption occurs at $Q_{ST} > 40$ kJ/mol). Despite the near 50% difference between the $Q_{ST}$ values between PTPA and SUPTPA (which would require repeat experiments to validate and analysis by Inductively Coupled Plasma Optical Emission spectroscopy (ICP-OES) to determine the N-content of SUPTPA and PTPA), both materials suitable for gas capture, since the physisorptive interactions are strong and regeneration of the material has a low energy penalty.

The accuracy of the technique used to determine $Q_{ST}$ described in this section can be improved by obtaining CO$_2$ isotherms at more temperatures. This can account for the appearance of the plots; typical $Q_{ST}$ plots have a small initial increase, followed by a gradual decrease in $Q_{ST}$ whereas this is not evident for SUPTPA. The $Q_{ST}$ value obtained for SUPTPA is almost half of that obtained for PTPA. However, as a result of the high CO$_2$ uptakes demonstrated by SUPTPA, and the similarities found in material characterisation between SUPTPA and PTPA, it was decided that SUPTPA was to be used for CO$_2$ reduction and blending.

The information presented in this section has both characterised and highlighted the
similarities of PTPA and SUPTPA. It was decided that this was sufficient evidence to use SUPTPA for CO₂ reduction and blending.

### 4.1.3 Polytriphenylamine for Electrochemical CO₂ Reduction

SUPTPA was bound to the surface of a glassy carbon electrode (GCE) using Nafion as a binder. Nafion is commonly used as a binder in the preparation of electrodes due to its high proton conductivity, making it suitable for ECO₂R.

Before measurements, it was important to convert inputted potentials (E\textsubscript{Ag/AgCl}) to the pH-independent reversible hydrogen electrode (RHE) scale. Potentials within the range of -1 ≤ V vs RHE ≤ 1 were investigated to keep within the electrochemical stability window of water.

\[
E\textsubscript{Ag/AgCl} = E\textsubscript{RHE} - E\textsubscript{0 Ag/AgCl} + 0.059 \cdot pH \tag{4.3}
\]

E\textsubscript{0 Ag/AgCl} is the reference potential of an Ag/AgCl reference electrode (-0.1976 V vs SHE) and pH is the electrolyte pH.

Due to the hydrophobic nature of SUPTA, gas bubbles would form on the GCE surface upon submersion. This would impact the current produced by the system, and could potentially lead to the measurement of current densities lower than what is true for SUPTPA. However, there is evidence indicating that the hydrophobic nature of some electrocatalysts for ECO₂R benefits the process due to the enhancement of gas capture at the electrode surface. Cyclic voltammograms for SUPTPA in Ar and CO₂ are shown in Figure 4.11
The cyclic voltammograms exhibit no noticeable redox peaks, showing that PTPA itself is not being oxidised and reduced. Its stability in the potential range investigated is supported by the lack of significant current drops throughout measurements.

The currents detected in the Ar-saturated electrolyte are marginally higher than those detected in the CO$_2$-saturated electrolyte at the extremes of the potential ranges investigated. Current density values increase at the potential window extremes investigated because of electrochemical processes such as HER occurring.

Similarly, the chronoamperograms show little difference in the current density between aqueous electrolytes. It is commonly observed that CO$_2$ reduction occurring on an electrode results in an impact, be it an increase or decrease, on the recorded current density when comparing signals recorded from the CO$_2$-saturated and inert gas-saturated electrolytes.\cite{122,125}
Results and Discussion

Figure 4.12: SUPTPA chronoamperograms.

Products were detected by NMR spectroscopy in the CO$_2$-saturated electrolytes. CO$_2$ was reduced to formate and methanol by SUPTPA at moderate Faradaic efficiencies. Product peaks were also observed, on a lesser scale, in the Ar-saturated electrolytes and is due to CO$_2$ captured during SUPTPA’s synthesis and from ambient air.

Using the NMR spectrum of the CO$_2$-saturated electrolyte following CA at -0.9 V (vs RHE) for SUPTPA as an example, products peaks could be highlighted, assigned and integrated to obtain the peak area.
Once the peak integrals were obtained, Equation 4.4 could be used to calculate the amount of product produced in mol.

\[
Product_{mol} = \frac{I_x \cdot 0.001 \cdot 10 \cdot 0.005}{N_x \cdot 600} \tag{4.4}
\]

\(I_x\) is the integral area of reduction product \(x\) (the numbers at the bottom of Figure 4.13) and \(N_x\) is the number of protons in reduction product \(x\) responsible for producing the peak. The numbers in Equation 4.4 are the concentration and volumes used in the NMR tube and H-cell. 0.001 is the concentration of the internal standard in mol/dm\(^3\), 10 and 600 are the volumes of the internal standard and electrolyte added to the NMR tube respectively in \(\mu\)L, and 0.005 is the volume of the catholyte in dm\(^3\). The value obtained is the amount of product produced in the catholytic side of the H-cell in moles which can be entered into Equation 1.17 to determine the Faradaic efficiency (FE) of the system.
Product formation is limited to C$_1$ products (formate and methanol). It is plausible that SUPTPA follows the reduction pathway suggested by Khezri et al. for group 3 catalysts, i.e. Cu. This is because both formate and methanol are produced in tandem.

During cell operation, bubbles forming on the surface of the PTPA-covered GCE were observed. This suggests that PTPA was forming some gaseous product during cell operation, be it hydrogen or a gaseous ECO$_2$R product such as CO. For full product analysis, a technique which allows for gaseous product measurement, such as differential electrochemical mass spectroscopy (DEMS) is required. This technique can be used to assign the amount of current responsible for each reduction product.

### 4.1.4 Blending Requirements

The material losses associated with powder sorbents for point-source capture presents the main issue with using SUPTPA on an industrial scale for ECO$_2$R. Further processing and additives such as the casting of the material onto a conductive substrate using a binder will also likely increase sorbent/catalyst cost.

This gives the motivation to blend SUPTPA with polymer support networks (PSNs). However, as indicated in Subsection 1.5.3, the loss of conductivity and blocking of ac-
tive sites could potentially translate to a loss of the ability to electrochemically reduce CO$_2$. The PSN should be selected based on its ability to provide good structural support, allow for high SUPTPA mass loadings and be processable so that electrode architecture can serve as a design parameter to prevent the loss of the properties which makes SUPTPA suitable for ECO$_2$R.

The following is a list of parameters and properties which were decided to be important in this investigation.

- Insoluble in water and CO$_2$ reduction products.
- Show ionic and electronic conductivity
- Be processable/printable
- Have a high surface area
- Be mechanically, thermally and chemically stable
- Have a high affinity for CO$_2$
4.2 Polyethylene Oxide-based Films

Polyethylene oxide (PEO) and PEO-containing block-copolymers are CO$_2$-philic polymers have shown promise in membrane applications for point-source carbon capture. This is a result of dipole-quadrupole interactions between the repeating ethylene oxide units and CO$_2$ molecules. Containing a redox-active, CO$_2$-philic polymer within a CO$_2$-philic, solution-processable membrane motivated this choice of material.

4.2.1 Hydrogels

PEO is soluble in water so a cross-linking mechanism had to first be established to prevent degradation of the electrode during ECO$_2$R tests in the aqueous electrolyte. Following the method outlined in Subsection 3.3.1, PEO with a $M_w$ of 1,000,000 was dissolved in water alongside polyvinyl alcohol (PVA) of $M_w$ 90,000. The repeating hydroxyl groups in PVA were cross linked by a dialdehyde in acidic conditions by the following mechanism to form a ketal.
This created a cross-linked PVA network which entangled long PEO polymer chains. Gels consisting of PVA and SUPTPA only were also formulated for a direct comparison of the impact of PEO presence in the composite during ECO₂R. The resulting polymer composite, shown in Figure 4.16, were hydrogels, swelling in the presence of water. Upon blending with SUPTPA, the hydrophobic CMP would be forced into contact with the electrolyte and therefore any dissolved CO₂.
In their dry state, the PEO-based composite was not conductive but after formulation in the acidic condition, the gels demonstrated a degree of ionic conductivity. It is suggested that this arose from the Grötthus mechanism, or ”proton-hopping” in which protons present in the cross-linked network are able to transfer from one water molecule to another.\footnote{Grötthus mechanism}

Since the gels were to be used in weakly alkaline conditions, the networks were dried and washed repeatedly with deionised (DI) water before subsequently being submerged and left to swell in the 0.1 M KHCO$_3$ electrolyte. A drop in conductivity was noticed following this. A different ionic conducting mechanism is suggested for hydrogels in alkaline conditions.

In alkaline conditions, the polymer chains exhibit an increased flexibility. In literature, this is commonly attributed to an increase in amorphicity of the polymer blend, indicated by an increase in the glass transition temperature (T$_g$) of the composite hydrogel. This increases the segmental motion of polymers in the electrolyte which in turn enhances the ionic conductivity of the material.\footnote{Amorphicity and T$_g$}

Conductance values were obtained using a 4-point probe. A 4PP consists of four equally- and narrowly-spaced probes. The two central probes act as a voltmeter and the two outer probes act as an ammeter. This measurement process is preferred over the 2-point probe method as it eliminates contact resistance between the probes and the sample, and reduces the internal resistance of the system.
The equation for resistivity, $\rho$, as measured by the 4PP is as follows.

$$\rho = \frac{\pi \cdot t}{\ln(2)} \cdot \frac{V}{T f_1 \cdot f_2} \quad (4.5)$$

$t$ is the sample thickness in m, $V$ is the voltage, $I$ is the current and $f_1$ and $f_2$ are geometric factors which account for the sample thickness and the length and width of the sample respectively. The conductance is simply the reciprocal of resistivity.

The geometric factors must be considered because the 4PP method assumes that the sample under analysis consists of an infinite array of positive and negative electric dipoles. To simplify this process, the hydrogels used for these measurements were formulated to have millimeter thicknesses as $f_1$ is equal to 1 as long as the sample thickness is less than the probe spacing, $s$. Once formulated, the gel’s diameters were measured.

To calculate $f_2$, cubic spline interpolation was conducted in MATLAB on tables of published geometric factors. Figure 4.17 depicts the conductance values for the gels which were investigated. Further work should be done to investigate the contributions of the electronic and ionic conductivity to the overall conductivity obtained.

Figure 4.17: Conductivity values for the hydrogels investigated.

The hydrogels PVA and PVA/PEO, PVA/SUPTPA and PVA/PEO/SUPTPA, corre-
spond to gels A, B, C and D in Table 3.2 respectively. As can be seen, the presence of PEO in the gels decreases their conductivity which can be explained by impeding the motion of protons via the Grötthus mechanism (acidic conditions) and impacting the segmental motion of the polymer chains (alkaline conditions).

The incorporation of SUPTPA into the gels had no statistically-significant effect on the conductivity of the overall composite in acidic conditions. This is highlighted by the error bars in Figure 4.17 which show 2 standard deviations of the average conductivity value. It is clear that in alkaline conditions, however, the gels containing SUPTPA were more conductive than the blank (gels containing no SUPTPA) gels.

SUPTPA is a polyaniline-based (PANI-based) CMP. As described in Subsection 1.3.2, PANI can adopt different redox activities and intrinsic conductivities through acid- and base-doping. Through being exposed to different conditions (i.e. the acidic environment via gel formulation and the weakly alkaline environment of 0.1 M KHCO₃), it is plausible that SUPTPA is reaching different redox states, however further work would be required to electrochemically characterise SUPTPA and confirm this theory. Table A.2) in the appendix show the raw conductivity values of the gels.

To ensure the gels were not degrading, blank gels were left soaking in the 0.1 M KHCO₃ electrolyte before the electrolyte was collected and an NMR spectrum was obtained of it. It was clear from this NMR that there were polymer chains in the material which had not been cross-linked due to the presence of a large peak in the chemical shift region of aliphatic molecules.

The presence of the glutaraldehyde (GA) cross linker also generated peaks which directly overlapped with those generated by formate and methanol; two products which have been shown to be produced by SUPTPA (the NMR spectrum of GA is in Figure A.31 in the Appendix). This can be seen in the green and purple regions highlighted in Figure 4.18, which were present despite careful washing of the composites.
Terephthalaldehyde (TPA), seen in Figure 4.19, was selected as another dialdehyde cross-linker to counteract these effects. However, gel degradation and peak overlapping was again observed (the NMR spectrum of TPA is in Figure A.32 in the appendix). It was therefore decided that these materials were not a suitable PSN for this application due to the interference they present with product detection.

Figure 4.19: Chemical structure of TPA.

4.2.2 Polyethylene Glycol Diacylate

To further investigate PEO-containing PSNs, polyethylene glycol diacrylate, a PEO-containing block co-polymer was investigated. In the presence of UV light and a photoinitiator, polyethylene glycol diacrylate (PEGDA) can be cross-linked by free-radical photopolymerisation. The initiation for this reaction is shown in Figure 4.20.
Results and Discussion

As can be seen from Section 3.3.1, many different compositions were formulated. However, the resulting composite was extremely brittle and non-conductive, making them poor material choices as a use for an electrode since electrical connections were difficult to establish. This is due to the high level of cross linking that occurred. The power of the UV lights within the reactor used in these studies was a factor of 100 higher than what is typically used in literature. The composite can be seen below in Figure 4.21.

These initial experiments highlighted the importance of using a PSN with good structural integrity, which does not degrade in the electrolyte and interfere with the NMR spectrum when identifying reduction products. Therefore, polypropylene was investigated as an alternative PSN.
4.3 Polypropylene Composites

Polypropylene (PP) is a commercial thermoplastic which shows excellent chemical stability and fatigue resistance. It is widely used for medical and food applications and, owing to its flowability, is commonly processed into filaments to be used for fused deposition modelling (FDM).

There is significant literature reporting the formulation of PP/carbonaceous material composites which exhibit enhancement of the mechanical, thermal, electrical, optical and structural properties of the pristine materials. The properties of PP, alongside its ability to accommodate high surface area materials within its structure motivated the choice for this PSN.

The formulation method described in Section 3.3.2 was provided by PhD student Sam Deeks, and was followed using SUPTPA. Figure 4.22 shows the composites once processed into filaments.

The limit to which SUPTPA could be added was found to be 30 wt% before the composite became too brittle for handling. Alone, this composite was not conductive so could not be used for ECO₂R. Carbon black (CB) and graphene nanoplatelets (GN) were explored as conductive additions to the composite.

Graphene is a single monolayer of graphite. It consists of a single layer of carbon atoms arranged in a two-dimensional honeycomb lattice. Its use in materials science is motivated by its high tensile strength and electrical conductivity. However, there is a lack of convenient mass-production techniques to produce defect-free graphene. GN are a hybrid between graphene and graphite (which consists of stacked sheets of graphene) and are widely available, exhibiting high electrical and thermal conductivity and mechanical stability. Due to the planar structure of graphene, and the layered structure of graphite, GN exhibit a plate-like morphology. This can be seen in Figure 4.23.
CB is another conductive, high surface area allotrope of carbon produced by the incomplete combustion of petroleum products. It is commonly blended with PP to yield a conductive polymer. There is evidence of a synergistic effect of using GN and CB in composites in which the presence of GN reduces CB agglomeration, and the spherical morphology of CB (seen in Figure 4.23) and the plate-like structure of GN improves the percolation network of the hybrid fillers, increasing the amount of conductive pathways within the PSN.\[213\]

![SEM images of CB and GN](image)

(a) CB, 5000x magnification.  
(b) CB, 20000x magnification.  
(c) GN, 5000x magnification.  
(d) GN, 20000x magnification.

Figure 4.23: SEM images of CB and GN (scale bar at 5000x magnification: 5\(\mu\)m, scale bar at 20000x magnification: 1\(\mu\)m)

The impact of CB and GN on the microstructure of PP was investigated by obtaining SEM images of the surfaces and cross sections of the formulated wires. GN imparts its plate-like morphology whilst CB created circular cavities and protrusions along the composite surface. Both the cross-sections of the composites and their surfaces feature cavities which may prove an advantage for catalysis, allowing for the electrolyte to reach
the internal structure of the electrode.

![SEM images of PP-15CB and PP-15GN](image)

(a) PP-15CB cross-section, 100x magnification.

(b) PP-15CB surface, 10000x magnification.

(c) PP-15GN cross-section, 80x magnification.

(d) PP-15GN surface, 2000x magnification.

Figure 4.24: SEM images of PP-15CB and PP-15GN (scale bar at 100x magnification: 100µm, scale bar at 10000x magnification: 1µm, scale bar at 80x magnification: 200µm, scale bar at 2000x magnification: 10µm.)

Conductivity tests were conducted on the 4PP. The shape of the PP wires meant that the equation to determine conductivity was simplified (Equation 4.6), because the geometric correction factors contributed negligibly to the overall conductance of the material.

\[
\rho = \frac{Vwh}{Il}
\]  

(4.6)

V and I are the voltage and current, determined from the gradient as before. w is the width of the filaments and h is the height of the filament measured in m (the filament mould was designed such that both w and h take the value of 0.001 m) and l is the length...
between the two points at which the voltmeter takes its measurement. Conductance values are shown in Table A.3 in the Appendix. Figure 4.25 depicts these values. As before, the error bars show 2 standard deviations of the dataset collected, and highlight that there is no overlap between the SUPTPA-containing composites and those which do not contain SUPTPA. This shows that SUPTPA improves the conductive network within the composite, perhaps providing a synergistic effect with the CB as described previously. 

Figure 4.25: PP composite conductances (N.B. a log transformation was used to represent this data to more accurately depict differences).

The CB-containing composites have the highest conductivity, despite the synergistic effect achieved by GN and CB reported in literature. All composites were tested for ECO$_2$R, including those which do not contain SUPTPA to act as baselines, ensuring that all activity towards ECO$_2$R was a result of SUPTPA and not CB or GN. As indicated in Section 1.4.3, little to no reduction products were expected for pure CB and GN composites due to lack of functionality and therefore low CO$_2$ capture selectivity.

Cyclic voltammograms and chronoamperograms were obtained for all composites (note that the conversion to RHE was incorrect for CV conducted on these composites, so meaningful conclusions could not be drawn from them). Cyclic voltammograms are shown in Figures A.7 to A.18 in the Appendices.
Results and Discussion

Chronoamperograms (shown in the Appendices, from Figure A.19 to Figure A.25) indicate different activities between the composites for ECO$_2$R. By comparing currents achieved during chronoamperometry between the Ar- and CO$_2$-saturated electrolytes, it can be inferred if the material is selective towards ECO$_2$R or the hydrogen evolution reaction (HER).

Following chronoamperometry, the electrolyte was collected and NMR spectra of the electrolytes were once again obtained to indicate the presence of reduction products (all NMRs obtained from the PP composites are shown in Figures A.45 to A.108. The FE to which the composites reduced CO$_2$ was calculated, and the values are compared in Figure 4.26.

Figure 4.26: FEs achieved by the PP composites.

Note that the necessity of conductive additions is highlighted by the chronoamperograms obtained of the PP-30SUPTPA composite (Figure A.25). The currents achieved were on the order of nA. This low current prevented sufficient electron flow for ECO$_2$R to occur, as no reduction products were detected for this composite.

Interestingly, the composites containing a mixture of CB and GN were the only composites showing a decrease in current density between chronoamperometry conducted in the Ar- and CO$_2$-saturated electrolytes (Figures A.23 and A.24). This is reflected by the low FEs achieved by these materials, suggesting the competing HER dominated the redox reactions occurring at the electrode surface. The charge passing through the electrode that was contributing to the ECO$_2$R reaction was low as a result.
The PP-15CB15SUPTPA composite shows the highest current densities of all composites, which would be expected from its high conductivity. This enhanced electron transfer, in comparison to other composites, clearly aided in the process of ECO$_2$R. As can be seen in Figure 4.26, this composite demonstrated the most consistent ECO$_2$R capabilities, and achieved a high FE towards formate at low overpotentials.

The incorporation of SUPTPA into the CB-containing materials enhanced the composite’s ability to reduce CO$_2$. Furthermore, whilst other materials such as the PP-7.5CB7.5GN15SUPTPA demonstrated the ability to reduce ECO$_2$R to methanol, this was in low quantities. As a result, the PP-15CB15SUPTPA composite was selected as the material to be printed into an electrode.

Following the procedure described in Section 3.3.2, PP-15CB15SUPTPA was formulated into a filament and printed into a mesh cylinder by fused deposition modelling (FDM). An electrode holder was also printed for the electrode by FDM.
Conductivity measurements were performed on the printed material to ensure that the process of printing had no significant effect on the composite’s properties. As can be seen in Table 4.3, there is no significant difference between these values.
Table 4.3: Comparison of printed and non-printed PP-15CB15SUPTPAn conductances.

<table>
<thead>
<tr>
<th>Composite</th>
<th>Conductance (S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-CB15SUPTPAn15</td>
<td>136.24</td>
</tr>
<tr>
<td>Print</td>
<td>146.57</td>
</tr>
</tbody>
</table>

Despite the similarities in conductivity, the increased amount by weight of SUPTPA partaking in ECO$_2$R and the intricate electrode design, the printed electrode was outperformed by the original filament composite in terms of ECO$_2$R as shown in Figure 4.28 (all NMRs obtained for the mesh electrode are shown in Figures A.109 to A.120). Furthermore, the printed electrode achieved lower current densities during cyclic voltammetry (CV) and chronoamperometry (CA) (Figures A.26 and A.27).

Figure 4.28: FEs achieved by the printed and non-printed PP-15CB15SUPTPAn composites.

To explain why the filament composite outperformed the printed electrode, SEM images were obtained comparing the microstructure of the printed and non-printed PP-CB15SUPTPAn15 composite.
There is a stark contrast in the microstructure between the printed and non-printed composite. Cavities are present in the cross section of the original PP-CB15SUPTPA15 composite. There is a fine dispersion of particles in the non-printed PP-CB15SUPTPA15 which were not present in the SEM image (Figure 4.24b) of the PP-CB15 composite surface. This is therefore assumed to be a fine dispersion of SUPTPA.

Figures 4.29c and 4.29d are extremely dark, which indicates that the printed electrode has very few surface features such as protrusions or cavities. This suggests that FDM impacts the microstructure of the material, since the finely dispersed particles on the electrode surface are only seen in the non-printed composite, and may be the reason for the drop in ECO$_2$R activity. It is well reported that the extrusion of polymeric materials results in anisotropic polymer orientation\cite{115}. The forces required for extrusion therefore
must force the polymeric binder into the pores of SUPTPA and CB, reducing cavities within the printed structure and therefore access of CO₂ into SUPTPA’s pores during ECO₂R.

N₂ porosimetry was conducted to further corroborate these findings. This required the evaluation of the thermal stability of PP-CB15SUPTPA15 by TGA due to the high temperature degassing stage.

![Graph showing weight retention rate as a function of temperature for PP-CB15SUPTPA15.](image)

Figure 4.30: Weight retention rate as a function of temperature for PP-CB15SUPTPA15.

Clearly the incorporation of CB and SUPTPA into PP is the reason for the weight retention for temperatures above 500 °C.

Following this, N₂ and CO₂ porosimetry was conducted on both materials. CO₂ isotherms are shown in Figure A.3. The N₂ isotherms are shown in Figure 4.31 and indicate that the materials possess extremely low surface area (< 20 m²/g). It should be noted that the Quantochrome Quadrasorb, the instrument used to take these measurements, is designed specifically for microporous, high surface area materials. This explains why the isotherms in Figure 4.31 are atypical of type II (i.e. macroporous) isotherms.
Figure 4.31: N$_2$ adsorption isotherms for printed and non-printed PP-CB15SUPTPA15.

The PSDs in Figure 4.32 show that the printed and non-printed PP-CB15SUPTPA15 composites are mesoporous, with some contribution from macropores. SUPTPA’s pores have been blocked as a result of blending owing to the lack of microporosity.
Results and Discussion

It was not possible to resolve the CO$_2$ heat of adsorption from the CO$_2$ isotherms. The surface areas of the composites and their CO$_2$ uptakes in wt% are shown in Table 4.4.

Table 4.4: Porosity and CO$_2$ uptake for printed and non-printed PP-CB15SUPTPA.

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface Area (m$^2$/g)</th>
<th>CO$_2$ uptake at 273 K (wt%)</th>
<th>CO$_2$ uptake at 298 K (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-CB15SUPTPA</td>
<td>16.0</td>
<td>1.3</td>
<td>2.3</td>
</tr>
<tr>
<td>PP-CB15SUPTPA Print</td>
<td>1.5</td>
<td>2.5</td>
<td>7.6</td>
</tr>
</tbody>
</table>

Both the CO$_2$ uptake and porosity of these materials is poor (the CO$_2$ adsorption isotherms obtained for the PP composites were conducted on a Quantachrome Quadrasorb which is designed for microporous materials, meaning the uptakes and surface areas may not be accurate). Despite this, with the SUPTPA exposed on its surface, the non-printed PP-CB15SUPTPA15 composite was able to reduce CO$_2$ selectively to formate at high FEs (91%) at a low overpotential. From this, a conclusion can be drawn.

The differences in activity between the printed and non-printed electrode is a result
of catalyst exposure. This highlighted the need for not only an electrically-conducting electrode, but one which maximised the exposure of the catalyst to the electrolyte, enhancing ion diffusion which is necessary for redox processes. SUPTPA contained within the PP-CB15SUPTPA15 composite will not contribute to ECO$_2$R since electrochemical reactions occur at the electrode surface.

The results from this section highlighted the need for a thin, electrically conducting and porous PSN to maximise the SUPTPA exposed. As a result, PIM-1, a polymer of intrinsic microporosity, was next to be investigated.
4.4 PIM-1 Composites

Polymers of intrinsic microporosity (PIMs) are a class of microporous materials developed in 2004 as a result of research led by Budd and McKeown. PIMs possess an amorphous nanoporous structure with high surface areas as a result of networks composed of rigid spirocyclic structures which do not pack space efficiently. The porosity that these materials exhibit is termed intrinsic as it arises solely from their molecular structure.

PIMs demonstrate that a network of covalent bonds are not required to produce a microporous organic material so, unlike conventional microporous materials, are processable by solvent-based techniques. Owing to this solution processability, PIMs have been widely investigated as gas separation and storage membranes. PIM-1, a type of PIM shown in Figure 4.33, is widely investigated for this purpose due to its high fractional free volume and good permeability.

![Image of PIM-1 in granule (a) and film (b) form.](image)

Figure 4.33: PIM-1 in granule (a) and film (b) form.
4.4.1 PIM-1 Synthesis and Characterisation

PIM-1 was synthesised by double aromatic nucleophilic substitution following the procedure outlined in Section 3.3.3. The reaction scheme is shown in Figure 4.34.

![Reaction scheme for PIM-1 synthesis](image1)

\[
\text{K}_2\text{CO}_3, \text{DMF}, 65^\circ\text{C}, 72\text{hrs}
\]

Figure 4.34: Reaction scheme followed for PIM-1 synthesis.

The reaction mechanism is shown in Figure 4.35.

![Reaction mechanism for PIM-1 synthesis](image2)

Yields are shown in Table 4.5. This simple, one-pot synthesis was suitable for electrode formulation, as amounts obtained were on the gram scale, providing sufficient material for testing and ink formulation.
Table 4.5: PIM-1 yields, surface areas and CO$_2$ uptakes.

<table>
<thead>
<tr>
<th>Material</th>
<th>Pellets</th>
<th>Film</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield (%)</td>
<td>77</td>
<td></td>
</tr>
<tr>
<td>Surface Area (m$^2$/g)</td>
<td>828$^{[3]}$</td>
<td>681$^{[3]}$</td>
</tr>
<tr>
<td>CO$_2$ Uptake at 273 K (wt%)</td>
<td>12</td>
<td>8.2</td>
</tr>
<tr>
<td>CO$_2$ Uptake at 298 K (wt%)</td>
<td>6.5</td>
<td>5.6</td>
</tr>
<tr>
<td>CO$<em>2$ Q$</em>{ST}$ (kJ/mol)</td>
<td>26.5</td>
<td>26.5</td>
</tr>
</tbody>
</table>

Note that the BET surface areas for the PIM-1 granules and film are reported from literature as they could not be confidently resolved from the isotherms obtained for them. The values that were recorded are shown in Table A.1 in the Appendix.

N$_2$ and CO$_2$ isotherms for the PIM-1 film are shown in Figures 4.41 and in the Appendix in Figure A.4. N$_2$ and CO$_2$ isotherms for the PIM-1 granules are shown in Figures 4.46 and in the Appendix in Figure A.5. PSDs are shown in Figure 4.51.

The high surface areas and high CO$_2$ uptakes are attributed to the intrinsic microporosity of PIM-1. Clearly, in the as-synthesised granular form, PIM-1 has greater porosity than its post-processed film form. This decrease in porosity is a result of the internal pore structure, highlighted in the SEM and backscattered electron (BSE) images (the theory behind BSE images is explained in greater detail in Subsection 4.4.2) in Figure 4.39.

![BSE image of PIM-1 granules internal morphology, 60x magnification.](image1)

![SEM image of PIM-1 film, 75x magnification.](image2)

Figure 4.36: BSE and SEM image of PIM-1 granules and film respectively (scale bar at 60x magnification: 200µm, scale bar at 75x magnification: 200µm.)
The structure of the PIM-1 granules allows access of gas to internal pores and therefore greater gas uptake via adsorption, therefore explaining the higher surface area and CO\textsubscript{2} uptakes seen in Table 4.3. As with SUPTPA synthesis, FTIR was used to ascertain whether PIM-1 synthesis ran to completion. The green band in Figure 4.37 indicates -OH disappearance and the orange band indicates the attenuation of the alkane C-H stretch at 2900 cm\textsuperscript{-1} for 3,3',3'-tetramethyl-1,1'-spirobiindane-5,5',6,6'-tetraol TMSBT. The blue band indicates attenuation of the C-F stretch at 1400 cm\textsuperscript{-1} and the pink band indicates attenuation of CN stretching at 2250 cm\textsuperscript{-1} for tetrafluoroterephthalonitrile (TFTPN).

![Figure 4.37: FTIR spectra for PIM-1 and monomers.](image)

Following the synthesis and characterisation, it was decided that this material was suitable for electrode materials for ECO\textsubscript{2}R.

### 4.4.2 PIM-1 Composite Electrodes for ECO\textsubscript{2}R

There are many examples in literature where PIM-1 composites are made through the incorporation of nanoparticles into the polymer matrix to improve the gas selectivity of PIM-1\textsuperscript{80,218,219} motivating the decision to incorporate SUPTPA into PIM-1 to produce porous polymer electrodes. As outlined in Section 4.3, CB provided the composites with the highest conductivity and the best ECO\textsubscript{2}R performance. Therefore, CB was used as a conductive additive to these composites.
The formulation of PIM-based composite electrodes initially followed the same procedure to produce PIM-1 films as outlined in Subsection 3.3.3. Since SUPTPA and CB do not dissolve in THF, the slow evaporation of the solvent required to yield high quality PIM-1 films allowed time for the additives to settle at the bottom of the film. Despite the use of a high-powered tip sonicator, CB aggregates were also present in the films which can be seen in Figure 4.38.

The aforementioned separation and agglomeration presented two issues: firstly, there were localised regions of the composites containing high contents of SUPTPA and CB, making the films brittle and prone to fracture and the distribution of SUPTPA inhomogeneous. Therefore, the loadings of CB and SUPTPA which were achievable using a PIM-1 matrix were lower than that of the PP matrices which proved to be more accommodating (i.e. 20 wt% of additives could be incorporated into PIM-1 before fracture, Table 3.7 whereas 30 wt% was achievable using the PP matrix, Table 3.5). The loading limits are illustrated in Figure 4.38.

![Figure 4.38: Comparison of PIM1-CB10SUPTPA10 and PIM1-CB15SUPTPA15 film, with CB agglomerates present.](image)

Secondly, separation leads to the previous issue presented with the PP matrices, in which SUPTPA contained internally within the composite is not exposed to the electrolyte, and the amount of SUPTPA exposed to the electrolyte is unknown. With the porous nature of the PIM-1 matrix, the effects of this issue is not expected to be as pronounced as it was in the PP support networks; a noticeable drop in ECO\textsubscript{2}R activity was noted for PP composites where there was noticeably less SUPTPA exposed on the composite surface (Figures 4.29).
Separation was confirmed by SEM and BSE images. Backscattered electrons are produced when an atom is bombarded with high energy electrons which are reflected, or backscattered, by the nucleus in an elastic scattering process. Once the electrons are detected, an image is returned in which regions of the investigated area containing higher Z materials appear brighter than materials containing lower Z materials. This is because backscattering occurs more strongly for higher Z nuclei.

![BSE image of PIM1-SUPTPA10CB10 cross-section, scale bar at 75x magnification: 200µm.](image)

Figure 4.39: BSE image of PIM1-SUPTPA10CB10 cross-section, scale bar at 75x magnification: 200µm.

Figure 4.39 indicates clear sedimentation of SUPTPA in the PIM-1 composite, with Br atoms responsible for the contrast as Br terminates SUPTPA polymer chains.

Further characterisation was conducted to clarify the suitability of the materials for ECO$_2$R and potential industrial application. The composite containing 10 wt% SUPTPA and 10 wt% CB was selected for further investigation as this was the maximum loadings of the catalyst and conductive additive before the composite was too brittle to handle. Both PIM-1 and PIM1-CB10SUPTPA10 demonstrated good thermal stability, which improved upon addition of SUPTPA and CB, as shown in Figure 4.40.
Results and Discussion

Figure 4.40: Weight retention rate as a function of temperature for composite film PIM1-CB10SUPTPA10 (sudden spikes in the graph are a result of benchtop agitation).

N$_2$ porosimetry was conducted to measure the surface area of the films and CO$_2$ adsorption isotherms were obtained to ascertain the CO$_2$ uptake of the materials. Comparing the isotherms (Figures 4.41 and A.4), surface areas and uptakes of the PIM-1 and PIM1-CB10SUPTPA10 composite indicates the impact of CB and SUPTPA addition to these materials.
The isotherm for the PIM-1 film appears to have low uptakes at low N₂ partial pressures. This may be a fault of the Quantachrome Quadrasorb used to take this measurement, as the desorption regime appears to be typical of an IUPAC type I isotherm. The isotherm could not be used to resolve the BET surface area of the PIM-1 film investigated so a literature value will be quoted for the purpose of this discussion.

Whilst the PIM1-CB10SUPTPA10 composite is composed of 3 microporous materials, a pore-blocking effect may be responsible for the drop in porosity witnessed when comparing the isotherm of a PIM-1 film and the PIM1-CB10SUPTPA10 composite. Pore blocking is reported in literature where the incorporation of single-walled carbon nanotubes (SWCNTs) into a metal-organic framework (MOF) sees a drop in the surface area but an increase in the degree of microporosity when comparing the isotherms and PSDs of the unmodified MOF and the MOF-SWCNT composite.

The SWCNTs reduce the pore width of the material by being situated in the pore openings of the MOF. The decrease in pore size and increase in micropore volume results in increased gas uptake for the composite as a result despite having a lower reported surface area.
Results and Discussion

Pore blocking is evident when comparing the PSDs of the PIM-1 film and the PIM1-CB10SUPTPA10 composite (Figure 4.42), their BET surface areas and CO₂ uptakes. CO₂ isotherms for PIM1-CB10SUPTPA10 are in the Appendix in Figure A.4.

Figure 4.42: Pore size distributions of PIM-1 films and PIM1-CB10SUPTPA10.

Table 4.6: PIM-1 film and PIM1-CB10SUPTPA10 surface areas, CO₂ uptakes and CO₂ heat of adsorptions.

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface Area (m²/g)</th>
<th>CO₂ uptake at 273K (%)</th>
<th>CO₂ uptake at 273K (%)</th>
<th>CO₂ Q&lt;sub&gt;ST&lt;/sub&gt; (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIM-1 Film</td>
<td>681</td>
<td>8.2</td>
<td>5.6</td>
<td>26.5</td>
</tr>
<tr>
<td>PIM1-CB10-SUPTPA10</td>
<td>233</td>
<td>8.9</td>
<td>5.6</td>
<td>27.0</td>
</tr>
</tbody>
</table>

The comparison of the PSDs depict the pore blocking effect of composite formulation of PIM-1 films, in that the contribution to the overall surface area of PIM1-CB10SUPTPA10 comes from pores less than 40 nm in width. The BET surface area of PIM1-CB10SUPTPA10 is lower than that of reported PIM-1 film values as seen in Table 4.6. Interestingly, the CO₂ uptakes and Q<sub>ST</sub> values are similar for both materials despite the difference in surface areas, indicating that the presence of N-rich SUPTPA continues to have a contribution to the adsorption properties of the composite.

PIM1-CB10SUPTPA10 conductivity was tested using a 4PP. Due to the separation
which is highlighted in Figure 4.39, the conductivity of the composite changed depending on the side of the film that was measured. The side which contained a high concentration of CB and SUPTPA was measured to have a conductivity of 0.553 S/m whilst the “top” of the film which contained little to no SUPTPA and CB was not conductive.

The contrast in conductivity depending on the side of the film presents issues for ECO\textsubscript{2}R in a H-cell set-up in that only part of the material will be able to partake in electron-transfer processes required for electrochemical reactions. However, the films were tested nonetheless for their ability to reduce CO\textsubscript{2}. 3D printing by direct ink writing (DIW) requires a viscous ink which will prevent particle sedimentation seen in Figure 4.39.

CV and CA was used to test PIM1-CB10SUPTPA10 for ECO\textsubscript{2}R. CV was conducted in the potential range -1 to 0 V vs RHE for 4 cycles and -1 to 1 V vs RHE for 16 cycles. The cyclic voltammograms are shown in the Appendix in Figures A.29 and A.30. Chronoamperograms are shown in the Appendix in Figure A.28.

NMR spectroscopy was used as before to detect the presence of reduction products following CA (NMRs of the PIM1-CB10SUPTPA10 are shown in Figures A.121 to A.132. FE\textsubscript{s} were calculated for each investigated potential. PIM1-CB10SUPTPA10 showed product selectivity to methanol, as shown in Figure 4.43.
Results and Discussion

Figure 4.43: ECO$_2$R FEs achieved by PIM1-CB10SUPTPA10.

PIM1-CB10SUPTPA10 appears to reduce CO$_2$ to methanol at low overpotentials (CO$_2$ is reported to be reduced to methanol at -0.38 V vs SHE at pH 7$^{[20]}$, with the highest efficiency at 90.1%, occurring at -0.5 V vs RHE at pH 6.81 for the composite. There is a clear increase and drop-off in efficiencies across the potential range investigated, suggesting at higher potentials, the electrons being transferred are being consumed in parasitic reactions such as the hydrogen evolution reaction (HER). It is plausible that PIM1-CB10SUPTPA10 follows the reduction pathway suggested by Khezri et al.$^{[134]}$ for the production of methanol.

Following the initial tests using the PIM-1 composite films, inks were formulated by the method outlined in Section 3.3.3. PIM-1 is soluble only in volatile solvents such as tetrahydrofuran (THF), chloroform and dichloromethane (DCM) which presents issues if the solution is to be printed by DIW.

As described in Subsection 1.5.1, a piston applies a pressure to a shear-thinning ink which passes through an Archimedes screw followed by a nozzle to be printed onto a substrate to yield intricate designs. Using an ink formulated purely of PIM-1 and THF led to clogging of the printer parts due to rapid evaporation of the volatile solvent.

Furthermore, using a binary polymer solution composed purely of PIM-1 and THF
has been reported to yield a dense microstructure within the material. A viscous ink is required for DIW for two reasons: firstly, that shape retention is possible once the material is ejected from the nozzle, and secondly, significant shrinkage does not arise from the evaporation of the solvent.

Concentrated PIM-1 inks yield dense microstructures which is non-ideal for mass transfer applications in which the PIM-1 composite electrodes will be used for. Therefore, inspiration for ink formulation was taken from Zhang et al.\textsuperscript{201} Findings from this study reported that a ternary polymer solution consisting of a polymer, solvent and high boiling point non-solvent (PIM-1, THF and dimethylacetamide (DMAc)) produced a micro/meso-/macroporous structure arising from spinodal decomposition of the ink.\textsuperscript{201}

Spinodal decomposition describes the mechanism by which a single thermodynamic phase spontaneously separates into two phases. As applied to the PIM-1 inks tested, evaporation of a small fraction of the volatile solvent (THF) shifts the composition of the ternary polymer solution across the limit of solubility PIM-1 has in the THF/DMAc mixture, forcing solidification and forming a network of interconnected meso-/macropores. This network is suitable for the use of electrodes for ECO\textsubscript{2}R since CO\textsubscript{2} must be adsorbed, making the process mass-transport-limited. Access of dissolved CO\textsubscript{2} into the pores may also be enhanced due to the presence of macropores.

The printing parts used were made of polyether ether ketone (PEEK) which is a polymer resistant to dissolution and swelling in many organic solvents at room temperature. Initial printing tests were conducted with PIM-1 alone to reduce any waste of SUPTPA. These printing tests were conducted with needles with a printing diameter of 0.2 mm.

Three inks were tested using polymer solutions containing PIM-1 only. The compositions of the inks are in Table 3.8 in Subsection 3.3.3. Ink J clogged the printer. Ink I was printable, and the quality of the improved depending on the substrate used (a paper substrate provided more grip for the ejected ink) and upon the development of the printing parameters used. However, layer adhesion was poor (Figure 4.44a).

It was possible to print ink K into simple squares upon the modification of printing parameters which best suited the ink used. The printing parameters are shown in Table 3.10. Figures 4.44a and 4.44b highlight the evolution of how the modification of the printing parameters improve the quality of the printed part.
Results and Discussion

(a) Progression of printing parameters using ink I.

(b) PIM-1 printed with ink K.

Figure 4.44: Simple PIM-1 squares printed by direct ink writing with a ternary polymer solution.

The transparency of PIM-1 films, shown in Figure 4.33b, is clearly not evident in these printed parts indicating that the spinodal decomposition of the ternary polymer solution used has had a clear impact on the microstructure of PIM-1. This is confirmed both by SEM imaging and porosimetry. The impact of printing on the microstructure is also evaluated using SEM imaging and porosimetry by analysing PIM-1 cast from ink K.
Results and Discussion

(a) SEM image of PIM-1 printed by DIW using ink K, 2,000x magnification.

(b) SEM image of PIM-1 printed by DIW using ink K, 10,000x magnification.

(c) SEM image of PIM-1 cast from ink K, 2,000x magnification.

(d) SEM image of PIM-1 cast from ink K, 10,000x magnification.

Figure 4.45: SEM images of PIM-1 printed and cast from ink K respectively (scale bar at 2,000x magnification: 10µm, scale bar 10,000x magnification: 1µm).

The microstructure of the printed and cast part of PIM-1 from ink K (Figure 4.45) clearly consists of an open, macroporous structure more typical of PIM-1 pellets than PIM-1 film (Figure 4.36b). There are also similarities in the microstructure of the printed and cast PIM-1 part. Visually, the printed part (Figure 4.45a and 4.45b) is less porous than the cast part (Figures 4.45c and 4.45d). These observations are confirmed by porosimetry analysis in Figure 4.46 and Table 4.7.
Figure 4.46: Comparison of the N\textsubscript{2} isotherms of PIM-1 granules and PIM-1 casted and printed from ink K.

Table 4.7: PIM-1 film, pellets and PIM-1 cast and printed from ink K surface areas, CO\textsubscript{2} uptakes and CO\textsubscript{2} heat of adsorptions.

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface Area (m\textsuperscript{2}/g)</th>
<th>CO\textsubscript{2} uptake at 273K (%)</th>
<th>CO\textsubscript{2} uptake at 298K (%)</th>
<th>CO\textsubscript{2} Q\textsubscript{ST} (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIM-1 Film</td>
<td>681</td>
<td>8.2</td>
<td>5.6</td>
<td>26.5</td>
</tr>
<tr>
<td>PIM-1 Pellets</td>
<td>828</td>
<td>12</td>
<td>6.5</td>
<td>27.0</td>
</tr>
<tr>
<td>K-PIM1 Print</td>
<td>472.9</td>
<td>7.9</td>
<td>4.6</td>
<td>18.7</td>
</tr>
<tr>
<td>K-PIM1 Cast</td>
<td>721.8</td>
<td>11.4</td>
<td>8.4</td>
<td>33.3</td>
</tr>
</tbody>
</table>

CO\textsubscript{2} isotherms for the K PIM-1 Print and K PIM-1 Cast are shown in the Appendix in Figures A.5 and A.6. The isotherms, surface areas, CO\textsubscript{2} uptakes and Q\textsubscript{ST} values indicate that, as with the PP composites, printing has an impact on the porosity of the printed material. It is again hypothesised that the forces associated with extrusion closes cavities and pores within the structure of the printed material.

Despite this, inks containing CB and SUPTPA were formulated to have greater control over electrode design and to prevent sedimentation of the insoluble species within the
Results and Discussion

As aforementioned in this section, despite aggressive sonication of the polymer solution, CB agglomerates were still present in the PIM-1 inks used, resulting in clogging of nozzles with an internal diameter of 0.2 mm. Therefore, nozzles with an internal diameter of 0.8 mm were used despite the reduction in resolution in which the electrodes could be printed to.

The printing parameters were kept the same as those shown in Table 3.10 in Subsection 3.3.3, apart from the pressures used to extrude the ink, which was increased from 0.1 mbar to 0.25 mbar on addition of CB and SUPTPA. As shown in Table 3.9 in Subsection 3.3.3, the amounts of CB and SUPTPA in the inks was also changed. This is due to high contents of SUPTPA and CB clogging the printer nozzle and preventing a continuous flow of the composite ink.

Inks containing 20 wt% of CB and SUPTPA clogged the printer nozzle. The content of insoluble material was reduced to 10 wt% in ink K-CB5SUPTPA5 which resulted in the most printable ink. The printed electrodes are shown in Figure 4.47a.

![Figure 4.47a: Rectangular electrode printed with ink K-CB5SUPTPA5.](image)

(a) Rectangular electrode printed with ink K-CB5SUPTPA5.

![Figure 4.47b: Complex electrode structure printed with ink K-CB5SUPTPA5.](image)

(b) Complex electrode structure printed with ink K-CB5SUPTPA5.

Figure 4.47: Electrodes printed with ink K-CB5SUPTPA5.

The printing parameters still require refining, as highlighted in the comparison between a simple and complex printed structure in Figure 4.47. Small prints with simple geometries are achievable, but larger prints with complex structures are not due to poor layer adhesion. This is a result of rapid solvent evaporation which reduces the ability of the separate layers to adhere. Figures 4.48 highlight this and show that distinct layers are still visible even in simple rectangular structures of PIM-1 prints.
Results and Discussion

(a) BSE image of PIM-1 printed with ink K, 50x magnification.

(b) BSE image of PIM-1 printed with ink K, 100x magnification.

Figure 4.48: PIM-1 printed with ink K (scale bar at 50x magnification: 500 µm, scale bar 100x magnification: 100 µm).

Furthermore, pore blocking as reported when porous materials are blended with a polymer matrix\textsuperscript{188,189} is evident in the electrodes printed with ink K-CB5SUPTPA5. The interconnected, porous structure of PIM-1 printed by DIW and cast from ink K shown in Figure 4.45 is not visible in electrode K-CB5SUPTPA5, as shown in Figure 4.49.

(a) BSE image of PIM-1 printed with ink K, 50x magnification.

(b) BSE image of PIM-1 printed with ink K, 43x magnification.

Figure 4.49: Electrode printed with ink K-CB5SUPTPA5 (scale bar at 43x magnification: 500 µm, scale bar 5000x magnification: 5 µm).

A high surface area would be expected for a composite containing 3 microporous materials. It is reported that microporous materials can situate themselves within the pore openings of the matrix, potentially increasing the degree of microporosity and improving gas uptake\textsuperscript{220} Surface area analysis indicates a decrease in the BET surface area of K-CB5SUPTPA5 when compared to PIM-1 printed by ink K, but an increase in CO\textsubscript{2} uptake.
(comparing the values in Tables 4.7 and 4.8), corroborating this theory and once again indicating that the incorporation of N-rich SUPTPA into the PIM-1-based composite improves CO$_2$ uptake. Surface area, CO$_2$ uptakes and CO$_2$ $Q_{ST}$ values are shown in Table 4.8.

Table 4.8: BET Surface area, CO$_2$ uptakes and CO$_2$ $Q_{ST}$ of K-CB5SUPTPA5.

<table>
<thead>
<tr>
<th>Surface Area (m$^2$/g)</th>
<th>CO$_2$ uptake at 273K (%)</th>
<th>CO$_2$ uptake at 298K (%)</th>
<th>CO$<em>2$ $Q</em>{ST}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>342.3</td>
<td>8.5</td>
<td>6.2</td>
<td>23.4</td>
</tr>
</tbody>
</table>

Comparing the N$_2$ isotherms of printed PIM-1, PIM1-CB10SUPTPA10 film and K-CB5SUPTPA5 in Figure 4.50 illustrates how spinodal decomposition improves the porosity of the K-CB5SUPTPA5 composite, but how pore blocking decreases the porosity of the material.

Figure 4.50: Comparison of the N$_2$ isotherms of printed PIM-1, K-CB5SUPTPA5 and PIM1-CB10SUPTPA10.

As seen in Figure 4.51, the electrode printed with ink K-CB5SUPTPA5 exhibits good macroporosity which may improve access of the electrolyte to SUPTPA during ECO$_2$R. These materials were attempted to be used as an electrode in the H-cell setup. However,
as a result of the reduction in CB content, they were non-conductive and therefore could not be used as an electrode.

Figure 4.51: Comparison of all PSDs of the investigated PIM-1 materials in this study.

As a result of the poor conductivity of the material, it is clear that the PIM1-CB10SUPTPA10 film is best used for this application. More time was required to improve the printing parameters and investigate methods to de-agglomerate CB in the PIM-1 inks to eventually print an electrode which is electrically conductive and could therefore be used as an electrode for ECO$_2$R.

Despite poor conductivity and non-optimal printing parameters for the printed version of the PIM-1 composite, the PIM1-CB10SUPTPA10 film was able to reduce CO$_2$ via a multi-electron reaction to methanol, a synthetic fuel compatible with many internal combustion (IC) engines, at low overpotentials and FEs up to 90.1%.

The high FEs and low overpotentials achieved by PIM1-CB10SUPTPA10 clearly seems an improvement on the unblended SUPTPA catalyst which uses a GCE support. In comparison, SUPTPA was able to reduce CO$_2$ to formate, a much more simple reduction pathway, at -0.5 V vs RHE with a FE of 55.1 %, and methanol at -0.9 V vs RHE with a FE of 22.8 %. However, it must be considered that the amount of SUPTPA contained within the PIM1-CB10SUPTPA10 composite (0.01 g) is much larger than the amount drop casted onto the GCE (approximately 0.0008 g on the GCE). More work should be done to quantify the amount of SUPTPA within the composite materials able to partake.
Results and Discussion

PIM1-CB10SUPTPA10 did not produce any formate, which can be attributed to the ability of PIM-1 to capture and store CO$_2$, promoting a triphasic environment and increasing the residence time of CO$_2$ in the vicinity of SUPTPA. This increase in residence time can provide more time for electron-transfer processes between SUPTPA and CO$_2$ to occur to yield ECO$_2$R products which require more complex reaction pathways.

The aforementioned issues with the PIM1-CB10SUPTPA10 film having dual-sided properties as a result of sedimentation of SUPTPA and CB (Figure 4.39) may actually prove to be an advantage if the composite is used in gas diffusion electrolysers (GDEs). Perry et al. found that a thin layer of PIM-1 over electroactive Cu was able to store CO$_2$ in a triphasic interface to facilitate the electrochemical reduction of CO$_2$ by the Cu catalyst. PIM-1 also maintained the hydrophobicity of the cathode chamber, preventing flooding of the GDE and prolonging electrode life.

The results reported by Perry et al. alongside the ability of PIM1-CB10SUPTPA10 to reduce CO$_2$ to methanol, highlight the promise porous polymers present in the field of ECO$_2$R.
Conclusions

The initial aims of this study were to formulate polymeric 3D-printable inks/filaments containing polytriphenylamine (PTPA), which could be 3D printed into electrodes for the application of electrochemical CO₂ reduction (ECO₂R). PTPA was successfully synthesised with high percentage yields (99.7 %) by Buchwald-Hartwig cross-coupling using a 1.5:1 core (tris(4-bromophenyl)amine) to linker (phenylenediamine) ratio. The synthesis was successfully scaled-up by 5 times to yield scaled-up PTPA (SUPTPA) to ensure a sufficient supply of material for blending.

PTPA and SUPTPA were subjected to multiple materials characterisation techniques to reveal good temperature resistance, π-conjugation, an amorphous structure and high degrees of microporosity. SUPTPA was used as a catalyst for ECO₂R using a glassy carbon electrode (GCE) support. Cyclic voltammetry (CV) and chronoamperometry (CA) were employed to electrochemically analyse SUPTPA, as well as produce reduction products for detection by nuclear magnetic resonance (NMR) spectroscopy. SUPTPA was found to reduce CO₂ to formate and methanol selectively, and product quantities and Faradaic efficiencies (FEs) were resolved using quantitative NMR.

3 polymers were identified as potential polymer support networks for SUPTPA based on their processability and affinity to CO₂. Once blending techniques were established, the composite materials were tested for ECO₂R, once again employing the same electrochemical techniques as before and using NMR spectroscopy to detect the presence of reduction products. Printing parameters were optimised for the inks/filaments to print high quality electrodes.

The polyethylene oxide-based composites showed the need for a chemically-resistant and structurally-sound support network. These findings were used to inform the choice of polypropylene as the subsequent support network to be investigated. Carbon black (CB) and graphene nanoplatelets (GN) were investigated as the conductive additives for these composites. CB-containing composites had the highest electrical conductivities and showed the highest activities for ECO₂R, once again yielding formate and methanol.

The PP-CB15SUPTPA15 composite was extruded into filaments to be used for 3D
printing. A complex electrode was printed which utilised the ability of thermoplastics to support overhangs during the printing process. The original PP-CB15SUPTPA15 composite outperformed the printed electrode; the extrusion forces associated with fused deposition modelling (FDM) removed cavities, blocking SUPTPA’s pores and therefore preventing access of SUPTPA to the CO₂-saturated electrolyte.

PIM-1, a polymer of intrinsic microporosity, was selected as the final support network to be investigated owing to its intrinsic microporosity, solution processability and ability to produce thin films. Sedimentation of SUPTPA and CB during film formation yielded a composite with dual-sided properties that was able to selectively reduce CO₂ to methanol at low overpotentials with high FE (-0.5 V vs RHE at 91.2 %).

Dimethylacetamide (DMAc) was used as a high boiling point non-solvent for PIM-1 (alongside tetrahydrofuran (THF), a volatile solvent for PIM-1) during direct ink writing (DIW) to slow down the rate of evaporation and produce an open, macroporous structure through the process of spinodal decomposition. Printing parameters were optimised for the ink so that simple, rectangular electrodes could be printed.

Owing to the reduction in CB content which was required for the successful printing of the PIM-1-based composite, the printed electrodes were non-conductive and could not be used for ECO₂R. PIM1-CB10SUPTPA10 shows good promise as a catalyst for ECO₂R and its dual-sided properties may prove useful for the use in a gas diffusion electrolyser (GDE) to promote a triphasic environment which increases the residence time of CO₂ within the vicinity of SUPTPA.
Future Work

The role carbon capture, storage and utilisation (CCUS) can potentially play in reducing global CO$_2$ emissions means that electrochemical CO$_2$ reduction (ECO$_2$R) catalysts and technology should be developed with an industrial scale in mind. Gas diffusion electrolysers (GDEs) are able to achieve industrially-relevant current densities and Faradaic efficiencies (FEs), a great improvement on the aqueous-phase electrochemical reactors which are commonly deployed in literature to test promising new ECO$_2$R catalysts.

Testing the PIM1-CB10SUPTPA10 composite in a GDE would therefore provide results that are more representative of how this material would behave if it were to be used for CCUS on an industrial scale.

Despite the loss of electrically-conducting properties as a result of direct ink writing (DIW), and decrease in porosity arising from extrusion forces, 3D printing still presents an interesting opportunity for the PIM-1-based composites investigated in this study. GDE cathode chambers can be flooded with the electrolyte if the electrode does not fit the tight geometric restraints of the gas diffusion layer (GDL). This renders the process mass-transport limited, reducing the efficiency of the ECO$_2$R process.

3D printing is a high-resolution processing technique which produces parts accurately to the dimensions specified. Therefore, optimisation for the printing of the PIM-1-based composites presented in this study is beneficial for the industrial-development of these materials.

Throughout the study, aqueous-phase products could only be detected as nuclear magnetic resonance (NMR) spectroscopy was the detection technique available. However, bubbles were observed on the cathodes during chronoamperometry (CA), suggesting gas evolving reactions were also occurring at the electrode interface.

There are other electrochemical techniques which can be deployed to characterise liquid and gaseous reduction products, such as in-situ differential electrochemical mass spectrometry. More information can be extracted from this technique to understand the reactions occurring at the electrode-electrolyte interface.
There are many reduction pathways that may occur during ECO\(_2\)R, and ECO\(_2\)R and the hydrogen evolution reaction (HER) may be occurring at the electrode surface simultaneously. Confidently knowing the amount of all products produced can be used to assign the amount of current passing through the electrode during CA/cyclic voltammetry (CV) to a specific reaction. More representative FE values will be obtained as a result. The activity of the composite materials can therefore be more confidently deduced.

Furthermore, there are reports of free-standing polyaniline-based (PANI-based) materials which have been 3D printed using dodecylbenzenesulfonic acid (DBSA), which acts as both a dopant and a binder to PANI. Since SUPTPA is a PANI-based CMP, it would be interesting to explore potential binders/dopants which simultaneously enhance processability and the electrochemical properties of SUPTPA.

During the study, it became clear that SUPTPA contained within the composite, and not on the electrode surface, was not able to partake in ECO\(_2\)R. This presented issues with confidently knowing the amount of electrochemically-available SUPTPA in the composites which prevented a direct comparison of the composite electrode performance with and SUPTPA-coated glassy carbon electrode (GCE).

Therefore, in future, it would be best to make electrode designs thinner and therefore higher surface area and less electrically-resistive, in the future. Particle size analysis such as dynamic light scattering, may also be used to obtain an average SUPTPA particle size. Using this value, assuming a homogenous dispersion of SUPTPA within the composite, and the surface area of the composite, an estimate of the amount of electrochemically-available SUPTPA can be made.

The final avenue to explore in the future will once again place an emphasis on the industrialisation of this CCUS technique. There is motivation to both capture and electrochemically reduce CO\(_2\) in-situ to remove any energy-intensive CO\(_2\)-regeneration steps and simplify the overall CCUS process.\[152\] This means that the process may be deployed for all types of carbon capture (i.e. both point-source and direct air capture (DAC)).

Therefore, it would be interesting to develop a system which investigates the capabilities of the composite materials to both capture and reduce CO\(_2\) in-situ.
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Appendices

A.1 Isotherms and BET Analysis

Figure A.1: PTPA and SUPTPA \( \text{CO}_2 \) adsorption at 273K.
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Figure A.2: PTPA and SUPTPA CO$_2$ adsorption at 298K.
Figure A.3: CO$_2$ adsorption isotherms for printed and non-printed PP-CB15SUPTPA15.

Figure A.4: CO$_2$ adsorption isotherms for PIM-1 film and PIM1-CB10SUPTPA10.
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Figure A.5: CO$_2$ adsorption isotherms for PIM-1 pellets and PIM-1 cast from ink K.

Figure A.6: CO$_2$ adsorption isotherms for PIM-1 printed from ink K and composite K-CB5SUPTPA5.
Table A.1: PIM-1 film and granules surface area, as measured by the Quantachrome Quadrasorb.

<table>
<thead>
<tr>
<th>PIM-1 Form</th>
<th>Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Granules</td>
<td>1104.21</td>
</tr>
<tr>
<td>Film</td>
<td>656.22</td>
</tr>
</tbody>
</table>
A.2 Conductance Values, Cyclic Voltammograms and Chronoamperograms

Figure A.7: Cyclic voltammogram of PP-CB15 composite with incorrect conversion.

Figure A.8: Cyclic voltammogram of PP-CB15 composite with incorrect conversion.
Figure A.9: Cyclic voltammogram of PP-CB15SUPTPA15 composite with incorrect conversion.

Figure A.10: Cyclic voltammogram of PP-CB15SUPTPA15 composite with incorrect conversion.
Figure A.11: Cyclic voltammogram of PP-GN15 composite with incorrect conversion.

Figure A.12: Cyclic voltammogram of PP-GN15 composite with incorrect conversion.
Figure A.13: Cyclic voltammogram of PP-GN15SUPTPA15 composite with incorrect conversion.

Figure A.14: Cyclic voltammogram of PP-GN15SUPTPA15 composite with incorrect conversion.
Figure A.15: Cyclic voltammogram of PP-CB15GN15 composite with incorrect conversion.

Figure A.16: Cyclic voltammogram of PP-CB15GN15 composite with incorrect conversion.
Figure A.17: Cyclic voltammogram of PP-CB7.5GN7.5SUPTPA15 composite with incorrect conversion.

Figure A.18: Cyclic voltammogram of PP-CB7.5GN7.5SUPTPA15 composite with incorrect conversion.
Figure A.19: Chronoamperograms obtained for the PP-CB15 composite.

Figure A.20: Chronoamperograms obtained for the PP-CB15SUPTPA15 composite.
Figure A.21: Chronoamperograms obtained for the PP/GN composite.

Figure A.22: Chronoamperograms obtained for the PP-GN15SUPTPA15 composite.
Figure A.23: Chronoamperograms obtained for the PP-CB15GN15 composite.

Figure A.24: Chronoamperograms obtained for the PP-CB7.5GN7.5SUPTPA15 composite.
Figure A.25: Chronoamperograms obtained for the PP-30SUPTPA composite.

Figure A.26: Cyclic voltammogram obtained for the PP-CB15SUPTPA15 printed electrode with the incorrect conversion.
Figure A.27: Chronoamperograms obtained for the PP-CB15SUPTPA15 printed electrode.

Figure A.28: Chronoamperograms obtained for the PIM1-CB10SUPTPA10 film electrode.
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Figure A.30: Cyclic voltammogram obtained for the PIM1-CB10SUPTPA10 printed electrode from -1 to 1 V vs RHE.
Table A.2: Conductivity values of the hydrogels investigated in this study.

<table>
<thead>
<tr>
<th>Hydrogel</th>
<th>Acidic Conductance (Ω)</th>
<th>σ</th>
<th>Alkaline Conductance (Ω)</th>
<th>σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA</td>
<td>0.018</td>
<td>0.0014</td>
<td>0.0009</td>
<td>0.0001</td>
</tr>
<tr>
<td>PVA/PEO</td>
<td>0.0088</td>
<td>0.0004</td>
<td>0.001</td>
<td>0.0001</td>
</tr>
<tr>
<td>PVA/SUPTPA</td>
<td>0.011</td>
<td>0.0009</td>
<td>0.005</td>
<td>0.0008</td>
</tr>
<tr>
<td>PVA/PEO/SUPTPA</td>
<td>0.0046</td>
<td>0.001</td>
<td>0.0052</td>
<td>0.0005</td>
</tr>
</tbody>
</table>

Table A.3: PP composite conductances with errors.

<table>
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<th>Composite</th>
<th>Conductance (S/m)</th>
<th>2 · σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-SUPTPA10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PP-SUPTPA20</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PP-SUPTPA30</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PP-CB15</td>
<td>7.10</td>
<td>0.28</td>
</tr>
<tr>
<td>PP-CB15SUPTPA15</td>
<td>136.24</td>
<td>38.87</td>
</tr>
<tr>
<td>PP-GN15</td>
<td>1.35</td>
<td>1.27</td>
</tr>
<tr>
<td>PP-GN15SUPTPA15</td>
<td>2.70</td>
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</tr>
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<td>39.00</td>
<td>5.66</td>
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A.3 NMRs

Figure A.31: $^1$H NMR spectrum of glutaraldehyde.
Figure A.32: $^1$H NMR spectrum of KHCO$_3$ electrolyte after exposure to terephthalaldehyde cross-linked gel.
Figure A.33: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.2 V vs RHE with a SUPTPA-coated glassy carbon electrode (GCE).
Figure A.34: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.2 V vs RHE with a SUPTPA-coated GCE.
Figure A.35: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.4 V vs RHE with a SUPTPA-coated GCE.
Figure A.36: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.4 V vs RHE with a SUPTPA-coated GCE.
Figure A.37: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.5 V vs RHE with a SUPTPA-coated GCE.
Figure A.38: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.5 V vs RHE with a SUPTPA-coated GCE.
Figure A.39: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.7 V vs RHE with a SUPTPA-coated GCE.
Figure A.40: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.7 V vs RHE with a SUPTPA-coated GCE.
Figure A.41: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.9 V vs RHE with a SUPTPA-coated GCE.
Figure A.42: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.9 V vs RHE with a SUPTPA-coated GCE.
Figure A.43: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -1.0 V vs RHE with a SUPTPA-coated GCE.
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Figure A.46: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.2 V vs RHE with a PP-CB15 electrode.
Figure A.47: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.4 V vs RHE with a PP-CB15 electrode.
Figure A.48: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.4 V vs RHE with a PP-CB15 electrode.
Figure A.49: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.5 V vs RHE with a PP-CB15 electrode.
Figure A.50: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.5 V vs RHE with a PP-CB15 electrode.
Figure A.51: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.7 V vs RHE with a PP-CB15 electrode.
Figure A.52: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.7 V vs RHE with a PP-CB15 electrode.
Figure A.53: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.9 V vs RHE with a PP-CB15 electrode.
Figure A.54: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.9 V vs RHE with a PP-CB15 electrode.
Figure A.55: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -1.0 V vs RHE with a PP-CB15 electrode.
Figure A.56: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -1.0 V vs RHE with a PP-CB15 electrode.
Figure A.57: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoa-mp-erometry conducted at -0.2 V vs RHE with a PP-CB15SUPTPA15 electrode.
Figure A.58: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.2 V vs RHE with a PP-CB15SUPTPA15 electrode.
Figure A.59: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.4 V vs RHE with a PP-CB15SUPTPA15 electrode.
Figure A.60: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.4 V vs RHE with a PP-CB15SUPTPA15 electrode.
Figure A.61: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.5 V vs RHE with a PP-CB15SUPTPA15 electrode.
Figure A.62: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.5 V vs RHE with a PP-CB15SUPTPA15 electrode.
Figure A.63: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.7 V vs RHE with a PP-CB15SUPTPA15 electrode.
Figure A.64: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.7 V vs RHE with a PP-CB15SUPTPA15 electrode.
Figure A.65: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.9 V vs RHE with a PP-CB15SUPTPA15 electrode.
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Figure A.66: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.9 V vs RHE with a PP-CB15SUPTPA15 electrode.
Figure A.67: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -1.0 V vs RHE with a PP-CB15SUPTPA15 electrode.
Figure A.68: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -1.0 V vs RHE with a PP-CB15SUPTPA15 electrode.
Figure A.69: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.2 V vs RHE with a PP-GN15 electrode.
Figure A.70: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.2 V vs RHE with a PP-GN15 electrode.
Figure A.71: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.4 V vs RHE with a PP-GN15 electrode.
Figure A.72: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.4 V vs RHE with a PP-GN15 electrode.
Figure A.73: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.5 V vs RHE with a PP-GN15 electrode.
Figure A.74: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.5 V vs RHE with a PP-GN15 electrode.
Figure A.75: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.7 V vs RHE with a PP-GN15 electrode.
Figure A.76: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.7 V vs RHE with a PP-GN15 electrode.
Figure A.77: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.9 V vs RHE with a PP-CB15SUPTPA15 electrode.
Figure A.78: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.9 V vs RHE with a PP-GN15 electrode.
Figure A.79: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -1.0 V vs RHE with a PP-GN15 electrode.
Figure A.80: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -1.0 V vs RHE with a PP-GN15 electrode.
Figure A.81: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.2 V vs RHE with a PP-GN15SUPTPA15 electrode.
Figure A.82: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.2 V vs RHE with a PP-GN15SUPTPA15 electrode.
Figure A.83: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.4 V vs RHE with a PP-GN15SUPTPA15 electrode.
Figure A.84: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.4 V vs RHE with a PP-GN15SUPTPA15 electrode.
Figure A.85: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.5 V vs RHE with a PP-GN15SUPTPA15 electrode.
Figure A.86: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.5 V vs RHE with a PP-GN15SUPTPA15 electrode.
Figure A.87: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.7 V vs RHE with a PP-GN15SUPTPA15 electrode.
Figure A.88: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.7 V vs RHE with a PP-GN15SUPTPA15 electrode.
Figure A.89: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoaamperometry conducted at -0.9 V vs RHE with a PP-CB15SUPTPA15 electrode.
Figure A.90: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.9 V vs RHE with a PP-GN15SUPTPA15 electrode.
Figure A.91: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -1.0 V vs RHE with a PP-GN15SUPTPA15 electrode.
Figure A.92: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -1.0 V vs RHE with a PP-GN15SUPTPA15 electrode.
Figure A.93: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.2 V vs RHE with a PP-CB7.5GN7.5 electrode.
Figure A.94: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.2 V vs RHE with a PP-CB7.5GN7.5 electrode.
Figure A.95: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.5 V vs RHE with a PP-CB7.5GN7.5 electrode.
Figure A.96: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.5 V vs RHE with a PP-CB7.5GN7.5 electrode.
Figure A.97: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.7 V vs RHE with a PP-CB7.5GN7.5 electrode.
Figure A.98: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.7 V vs RHE with a PP-CB7.5GN7.5 electrode.
Figure A.99: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -1.0 V vs RHE with a PP-CB7.5GN7.5 electrode.
Figure A.100: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -1.0 V vs RHE with a PP-CB7.5GN7.5 electrode.
Figure A.101: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.2 V vs RHE with a PP-CB7.5GN7.5SUPTPA15 electrode.
Figure A.102: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.2 V vs RHE with a PP-CB7.5GN7.5SUPTPA15 electrode.
Figure A.103: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.5 V vs RHE with a PP-CB7.5GN7.5SUPTPA15 electrode.
Figure A.104: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.5 V vs RHE with a PP-CB7.5GN7.5SUPTPA15 electrode.
Figure A.105: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.7 V vs RHE with a PP-CB7.5GN7.5SUPTPA15 electrode.
Figure A.106: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.7 V vs RHE with a PP-CB7.5GN7.5SUPTPA15 electrode.
Figure A.107: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -1.0 V vs RHE with a PP-CB7.5GN7.5SUPTPA15 electrode.
Figure A.108: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -1.0 V vs RHE with a PP-CB7.5GN7.5SUPTPA15 electrode.
Figure A.109: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.2 V vs RHE with a PP-CB15SUPTPA15 printed electrode.
Figure A.110: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.2 V vs RHE with a PP-CB15SUPTPA15 printed electrode.
Figure A.111: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.4 V vs RHE with a PP-CB15SUPTPA15 printed electrode.
Figure A.112: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.4 V vs RHE with a PP-CB15SUPTPA15 printed electrode.
Figure A.113: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.5 V vs RHE with a PP-CB15SUPTPA15 printed electrode.
Figure A.114: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.5 V vs RHE with a PP-CB15SUPTPA15 printed electrode.
Figure A.115: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.7 V vs RHE with a PP-CB15SUPTPA15 printed electrode.
Figure A.116: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.7 V vs RHE with a PP-CB15SUPTPA15 printed electrode.
Figure A.117: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.9 V vs RHE with a PP-CB15SUPTPA15 printed electrode.
Figure A.118: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.9 V vs RHE with a PP-CB15SUPTPA15 printed electrode.
Figure A.119: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -1.0 V vs RHE with a PP-CB15SUPTPA15 printed electrode.
Figure A.120: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -1.0 V vs RHE with a PP-CB15SUPTPA15 printed electrode.
Figure A.121: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.2 V vs RHE with a PIM1-CB10SUPTPA10 electrode.
Figure A.122: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.2 V vs RHE with a PIM1-CB10SUPTPA10 electrode.
Figure A.123: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.4 V vs RHE with a PP-CB15SUPTPA15 printed electrode.
Figure A.124: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.4 V vs RHE with a PIM1-CB10SUPTPA10 electrode.
Figure A.125: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.5 V vs RHE with a PIM1-CB10SUPTPA10 electrode.
Figure A.126: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.5 V vs RHE with a PIM1-CB10SUPTPA10 electrode.
Figure A.127: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronamperometry conducted at -0.7 V vs RHE with a PIM1-CB10SUPTPA10 electrode.
Figure A.128: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronomperometry conducted at -0.7 V vs RHE with a PIM1-CB10SUPTPA10 electrode.
Figure A.129: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.9 V vs RHE with a PIM1-CB10SUPTPA10 electrode.
Figure A.130: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -0.9 V vs RHE with a PIM1-CB10SUPTPA10 electrode.
Figure A.131: $^1$H NMR spectrum of Ar-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -1.0 V vs RHE with a PIM1-CB10SUPTPA10 electrode.
Figure A.132: $^1$H NMR spectrum of CO$_2$-saturated KHCO$_3$ electrolyte following chronoamperometry conducted at -1.0 V vs RHE with a PIM1-CB10SUPTPA10 electrode.