Electrochemical capture and conversion of carbon dioxide in acetonitrile using quinones

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**ELECTROCHEMICAL CAPTURE AND CONVERSION OF
CARBON DIOXIDE IN ACETONITRILE USING QUINONES**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2020

ELECTROCHEMICAL CAPTURE AND CONVERSION OF CARBON DIOXIDE IN ACETONITRILE USING QUINONES

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for the
degree of Master of Science

2020

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Abstract

The rising levels of CO₂ concentration in our atmosphere is one of the pressing issues faced to date as it can drive global environmental changes which could affect our livelihoods. In this work, quinones were investigated for their suitability as electrocatalysts for CO₂ capture and conversion. Quinones are well known for their binding affinity to electrophiles in their reduced form, and the ability to modify and add substituents onto quinones to alter their electronic and steric properties allow them to be versatile as an electrocatalyst. 1,4-Naphthoquinone (NQ) was found to be a potentially suitable electrocatalyst due to its ability to capture and react with CO₂. A hydrogen donor is suspected to be produced during the electrochemical cycling of NQ in the presence of CO₂ based on the decrease in the potential separation of the quinone reduction processes i.e. $\Delta E^{\text{red}} = |E_{Q1} - E_{Q2}|$ (where E_{Q1} was the first reduction potential and E_{Q2} was the second reduction potential). The formation of different intermediates was also determined using UV-Visible spectroscopy when NQ is reduced in the absence and presence of CO₂. Other quinones were also investigated but they did not appear to show as much promise as NQ as an electrocatalyst.

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Chapter 1

Introduction

1.1 Background Information

1.2 Objectives

1.3 Rationale

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1.1 Background Information

Since the Industrial Revolution, energy consumption from humans¹ and deforestation processes² have caused a rapid increase in the atmospheric concentration of CO₂ and other greenhouse gases. This excessive anthropogenic CO₂ emission result in the ‘greenhouse effect’, which is the additional retention of thermal infrared radiation by the atmosphere, causing the mean global temperature on the Earth’s surface to increase.³ The ‘greenhouse effect’ is known to drive global environmental changes such as a rise in sea levels,⁴ increase in occurrences of extreme weather events⁵ and a loss in the balance of the Earth’s eco-systems.³ In order to mitigate the emission of industrial CO₂, the Paris Agreement was adopted in 2015 by countries participating in the United Nations Framework Convention on Climate Change (UNFCCC). The Paris Agreement’s objective is to maintain the average global temperature rise to below 2 °C with respect to the pre-industrial levels, and to work towards limiting the rise to 1.5 °C.⁶ However, about two-thirds of the available budget have already been utilized, and the growing trends of CO₂ emission indicate that more effective solutions are needed to address this issue.⁷ Therefore, drastic and green practices must be explored and adopted by various countries and their respective authorities to achieve a balance between anthropogenic CO₂ emissions and its removal.

An alternative to fossil fuel consumption is the use of renewable energy which includes solar, wind, geothermal and hydropower. Even though the use of renewable energy is growing exponentially, it is still too low to offset the growth in fossil fuel consumption. In the US, renewable energy harvested accounts for only 7% of the total energy supply.⁸ Limitations in renewable sources such as low tidal currents, absence of geothermal hotspots and low wind speed restrict the efficient production of wind, geothermal and hydroelectric energy, which contributes to the dependence on carbon-based fuels.⁹ Despite its tropical climate, the utilization of solar energy in Singapore is affected by seasonal haze from neighbouring countries and intermittent cloud cover, limiting its usability.¹⁰ Apart from renewable energy, nuclear energy presents a large energy source with lower greenhouse gas emission. However, nuclear energy is non-renewable

and it comes with safety and security concerns as well as costly waste disposal, making it less reliable and limits its usage.¹¹

Decreasing the atmospheric CO₂ levels is a pressing issue and several approaches have been reported to mitigate the adverse effects of CO₂ emission on global climate patterns. A few of the strategies that have been investigated is the use of carbon capture and sequestration¹² and reutilization¹³. However, the process of carbon capture and sequestration only separates CO₂ gas from the gas feed for subsequent disposal into environmentally active carbon pools such as the ocean and several oil and gas sites.¹⁴ The energy and cost required for the process are large and results in a loss in energy efficiency instead.¹⁵ Thus, the recycling of CO₂ molecules is more advantageous as it can be utilized as a chemical feedstock for industrial process, storage medium for renewable energy and as a solvent or working fluid.¹⁶

The recycling of CO₂ can be achieved through electrochemical methods where a potential is applied across two electrodes to electrochemically reduce CO₂. The conversion of CO₂ can be performed either directly or indirectly. In direct electrochemical reduction, CO₂ gas is dissolved in the selected solvent and a potential is applied to induce the electrochemical reduction of the gas. Some advantages of using direct electrochemical reduction methods include the compatibility to pair with renewable energy sources, ability to operate experiments under standard temperature and pressure conditions, and the ease of reaction control through modifying external variables such as the material of the working electrode, type of electrolyte used and the voltage applied.¹⁷ A number of products such as methane, ethylene, formic acid, carbon monoxide and methanol have been reported to be produced from the direct electrochemical reduction of CO₂ with various experimental parameters such as the reaction medium, catalyst material and electrode configurations.¹⁸ Nonetheless, using direct electrochemical methods have several drawbacks such as high cost of using low abundance metals as the working electrode, low selectivity of products formed and a high potential of -1.9 V vs. SHE ¹⁹ required.²⁰

In indirect electrochemical reduction of CO₂, a co-reagent or an electrocatalyst is added to the system to aid in the reduction of CO₂. Organic compounds such as pyridinium²¹ and pyridoxine,²² inorganic metal complexes such as palladium,²³ manganese,²⁴ copper²⁵ and even microorganisms²⁶ have been examined on their capabilities of CO₂ reduction. These co-reagents are typically easier to reduce than CO₂ gas itself, and therefore may undergo either a pure electron transfer reaction or a chemical reaction with CO₂. The presence of an efficient electrocatalyst overcomes the high thermodynamic and kinetic barriers, thus lowering the reduction potential and enhances the overall efficiency of the system¹⁹. One of the greater challenges encountered in CO₂ reduction is the combination of efficiency and selectivity of the product even with the use of an electrocatalyst or co-reagent. The efficiency and selectivity have to be sufficiently high for practical use and simultaneously exhibit low overpotentials with large current densities required for applications in industries.²⁷ Currently, commercial electrolyzers used for the generation of chemical products, such as electrolyzing water to obtain hydrogen gas, typically operate at over 70% efficiency with current densities above 200mA cm⁻².²⁸ These values are an aim to work towards during the development of CO₂ electrocatalysts.

1.2 Objectives

In this thesis, quinones have been selected as the electrocatalyst of study for CO₂ reduction. Studies have shown that quinones can function as a molecule for carbon capture and separation²⁹ and used in applications for energy storage³⁰ due to the interactions formed between quinones and CO₂. Thus, the objectives of this thesis are to understand the mechanism of the electrochemical reduction of various quinones in the presence of CO₂ by isolating and characterizing intermediates and products.

1.3 Rationale

Quinones were chosen as the electrocatalyst of this study as they are well-known for their high-binding affinity to electrophiles in their reduced form^{29a, 31}. Their electrochemical behaviour is significantly different in the absence and presence of CO₂ in organic solvents, which would make identifying the presence of a reaction easier. Quinones are found in biological systems, such

as the photosynthetic pathway where the quinones function as effective electron carriers.³² By leveraging on this property, quinones could be utilized to lower the energy barrier required for the reduction of CO₂. The reduction of quinones follow an EE reduction mechanism (where E denotes an electron transfer reaction) to produce a radical anion or semiquinone (Q^{•-}) at potential E_{Q1} , followed by the generation of an aromatic dianion (Q²⁻) at a more negative potential E_{Q2} .³³ (Scheme 1)

Scheme 1. Electrochemical EE reduction mechanism of 1,4-naphthoquinone in aprotic organic solvents.

The voltammetric response associated with the reactions in Scheme 1 is shown in the cyclic voltammetry (CV) traces (voltammograms) in Figure 1, where 1,4-naphthoquinone (NQ) was used as an example. The peak heights for the two forward cathodic processes ($i_p^{\text{red}(1)}$ and $i_p^{\text{red}(2)}$) are similar since both processes involve the same number of electrons (i.e. one-electron). Additionally, the peak currents for the forward and reverse anodic process in each reduction reaction are approximately equal, thereby showing that the reduction of NQ is chemically reversible on the timescale of the CV experiments (~ seconds)

Figure 1. CVs of 1 mM NQ/0.1 M $n\text{Bu}_4\text{NPF}_6$ in acetonitrile (CH_3CN) recorded at 0.1 V s^{-1} scan rate with a 1 mm diameter planar glassy carbon (GC) working electrode (WE) at $25 \pm 2^\circ \text{C}$ under Ar conditions.

For fast electron transfer reactions, the theoretical value of the peak-to-peak separation (E_{pp}) between the cathodic and anodic peaks for a single redox couple is $\frac{57}{n} \text{ mV}$ (where n = the number of electrons transferred per molecule in the redox reaction).³⁴ In this case, the E_{pp} for the first redox couple ($\text{Q}/\text{Q}^{\bullet-}$) is 68.36 mV and 70.8 mV for the second redox couple ($\text{Q}^{\bullet-}/\text{Q}^{2-}$). Both values are fairly close to the theoretical value, suggesting that both electron transfer steps are electrochemically reversible (i.e. fast heterogeneous electron transfer between the electrode and the quinone in solution.) The difference observed for the experimental E_{pp} -value compared to the theoretical value is likely due to the effects of uncompensated solution resistance.

In the presence of dissolved CO_2 in a suitable aprotic organic solvent such as CH_3CN , most quinones will exhibit a single reduction peak as shown in Figure 2 (red trace).

Figure 2. CVs of 1 mM NQ/0.1 M $n\text{Bu}_4\text{NPF}_6$ in CH_3CN in the absence and presence of CO_2 (and in the absence of dissolved O_2) recorded at 0.1 V s^{-1} scan rate with a 1 mm diameter planar GC WE at $25 \pm 2 \text{ }^\circ\text{C}$.

The single peak has a reduction potential close to E_{Q1} (which is the first reduction potential of the quinone under conditions where molecular oxygen has been excluded from the solution (by purging with Ar gas)) and its peak height is also approximately doubled (in the presence of CO_2). There is also the disappearance of the second one-electron reduction peak at E_{Q2} . These observations indicate that the presence of CO_2 causes a shift of the second reduction potential E_{Q2} to less negative potentials at a value that is either equal to or less negative than E_{Q1} . The shift in the second reduction peak only occurs in the presence of CO_2 , which can serve as an indicator that a reaction has occurred between the reduced quinone species and CO_2 . The closeness of the potential of the single two-electron reduction process in the presence of CO_2 (red trace) compared to the first electron reduction process in the absence of CO_2 and molecular oxygen (black trace) also suggests that the neutral quinones is unaffected by the presence of CO_2 . This observation is also well documented for various other quinones such as 9,10-phenanthraquinone and 1,2-naphthoquinone.³⁵ However, it should be noted that not all quinones display such behaviour in the presence of CO_2 .

Figure 3. CVs of 1 mM chloranil (CQ)/0.1 M $n\text{Bu}_4\text{NPF}_6$ in CH_3CN in the absence and presence of CO_2 recorded at 0.1 V s^{-1} scan rate with a 1 mm diameter planar GC WE at $25 \pm 2^\circ \text{C}$.

Chloranil (CQ) is one such example where in the presence of CO_2 , two reduction peaks are observed instead of a single peak. CQ contains chlorine atoms which are electron-withdrawing, thus decreasing the nucleophilicity of the quinone and reduces its ability to interact with CO_2 within the CV time scale. This data has also led us to take into account the nucleophilic properties of a quinone when choosing one as a suitable electrocatalyst.

Quinones can be modified with different substituents (Figure 4) to alter their electronic and steric properties. This can stabilize the intermediates formed and lower their reduction potential, or increase their affinity to CO_2 and improve their bonding strength and reaction kinetics with CO_2 . Several factors were considered when selecting the quinones to use for this study, one of which is the electron affinity of the quinone. Having a greater electron affinity lowers the energy required to reduce the quinone, hence, reducing the energy required for CO_2 reduction. In order for a reaction to occur with CO_2 , the nucleophilicity of the quinone was also taken into consideration. A quinone that is more nucleophilic is more likely to attack CO_2 , which helps to drive the reaction forward and reduce the energy input required for the reaction to take place. Fine tuning of these properties can be achieved through the addition of electron-donating or

electron-withdrawing substituents and aromatic rings to the extended pi-framework, making quinones a versatile molecule to work with as an electrocatalyst.

Figure 4. Commonly available quinone. *Denotes naturally occurring quinone.

In this study, the reduced forms of quinones ($Q^{\bullet-}$, Q^{2-}) were utilised with the aim of capturing CO_2 and subsequently converting it into a beneficial compound such as alcohols or gases such as carbon monoxide. A non-aqueous medium was chosen due to the favourable solubility of CO_2 in non-aqueous solvents as compared to water (Table 1). Furthermore, quinones exhibit a simpler electrochemical behaviour in the aprotic organic solvents and are also more reactive due to the lack of hydrogen bonding (with water molecules) on the oxygen atom for stabilization in all three forms of the quinone. (Q , $Q^{\bullet-}$, Q^{2-}). Other solvent properties such as the electrochemical potential window was considered and explained in the later sections.

Table 1. Solubility of CO₂ gas in various solvents at 298 K and 1 atm³⁶

Solvent	CO ₂ concentration / mol L ⁻¹
Water	0.033
Methanol	0.060
Dimethylsulphoxide (DMSO)	0.135
Propylene Carbonate (PPC)	0.140
<i>N,N</i> -Dimethylformamide (DMF)	0.175
Tetrahydrofuran (THF)	0.211
Acetonitrile (CH ₃ CN)	0.280

Scheme 2 depicts the proposed reaction scheme involving the electrochemical capture and conversion of CO₂ using quinones.

Scheme 2. Proposed CO₂ capture and conversion mechanism using NQ.

Ideally in this proposed scheme, quinones can undergo a two-electron reduction to yield carboxylated dianions in the presence of CO₂, either as Q(CO₂)²⁻ or Q(CO₂)₂²⁻. Upon reaction, the quinone electrocatalyst can be regenerated and CO₂ can be converted into useful materials such as alcohols or hydrocarbons. Through this catalytic conversion system, it was hoped that the harmful

impacts of excess CO₂ on the environment would be reduced while generating useful products for further consumption.

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Chapter 2

Literature Review for CO₂ Reduction

2.1 Overview

2.2 Homogeneous Catalysts

2.2.1 Transition-Metal Complexes

2.2.2 Organic Catalysts

2.3 Current Studies on Quinones

2.4 Research Gap

References

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2.1 Overview

Among the many energy objectives that are currently present, the reduction of atmospheric CO₂ is a major issue at hand. Ideally, the CO₂ produced from industrial processes and fuel consumption will be negated by plants during photosynthesis so that the atmospheric CO₂ levels remain constant in order to maintain the stability of the environment. However, the increase in energy consumption for anthropogenic activities has led to the disruption of this balance, resulting in the increase in CO₂ and the “greenhouse effect”, making global warming an important issue to tackle today. Therefore, efforts to reduce CO₂ production and convert CO₂ into useful materials such as alcohols and hydrocarbons would seem to be necessary moves in order to prevent serious climate change.

One of the most attractive solutions in resolving the high levels of atmospheric CO₂ involves the capture and conversion of CO₂ into chemicals and fuels.¹ However, the process of converting CO₂ into useful materials still requires a significant input of energy. Table 1 shows the potentials (vs. the standard hydrogen electrode, SHE, at pH 7 in aqueous solutions) of the various products that can be formed from CO₂ reduction depending on the number of electrons and protons transferred.² Although some of the reactions are thermodynamically more favourable than the competing hydrogen evolution reaction (HER), the kinetics of CO₂ reduction is still rather slow. In order for product formation to occur, the linear CO₂ structure has to be first converted to a bent CO₂ anion radical (CO₂^{•-}).³ This step occurs at a redox potential of -1.9 V (vs. SHE at pH 7 in aqueous solutions)⁴ which is highly unfavourable. Thus, catalytic strategies have been in development to reduce CO₂ at lower energetic costs.

Table 1. Standard electrochemical potentials for CO₂ reduction in aqueous solution.

Reduction Potentials of CO ₂	E ⁰ / V vs. SHE at pH 7
CO ₂ + e ⁻ → CO ₂ ^{•-}	-1.90
CO ₂ + 2H ⁺ + 2e ⁻ → HCOOH	-0.61
CO ₂ + 2H ⁺ + 2e ⁻ → CO + H ₂ O	-0.52
CO ₂ + 4H ⁺ + 4e ⁻ → HCHO + H ₂ O	-0.51
CO ₂ + 6H ⁺ + 6e ⁻ → CH ₃ OH + H ₂ O	-0.38
2CO ₂ + 12H ⁺ + 12e ⁻ → C ₂ H ₄ + 4H ₂ O	-0.34
CO ₂ + 8H ⁺ + 8e ⁻ → CH ₄ + H ₂ O	-0.24
2H ⁺ + 2e ⁻ → H ₂	-0.42

2.2 Homogeneous Catalysts

The use of homogeneous catalysts is one of the methods for the indirect electrochemical reduction of CO₂. The transfer of electrons between CO₂ and the electrode occur homogeneously with the help of the catalyst that functions as a ‘mediator’. Reduction occurs at the catalyst’s reduction potential instead of the CO₂ reduction potential, therefore it is crucial that the reduction potential of the catalyst is less negative than that of CO₂ so that the catalytic system is energy efficient.⁵ The advantageous of using homogeneous electrocatalysts for CO₂ reduction include allowing better studies of the structure-reactivity relationship in order to enhance the product selectivity, and the reactions can be performed under milder conditions since electrolysis is conducted at less negative potentials.⁶

2.2.1 Transition-Metal Complexes

Transition-metal-based molecular complexes (e.g. Fe-, Co-, Cu- Mn-, Ni-, Cu-, Ru-, and Re-based complexes) have been studied in order to utilise them for catalysing the electrochemical reduction of CO₂. Fe complexes have been more frequently studied for CO₂ reduction, and the Fe porphyrin complexes have made tremendous progress in terms of its ligand optimisation and is one of the best-characterised systems. Savéant and co-workers were the first group to perform

studies on the Fe tetraphenyl porphyrin complex (**1**, $[\text{Fe}^{\text{III}}(\text{tpp})]\text{Cl}$).⁷ The catalyst was found to be able to convert CO_2 into CO at a potential of -1.6 V vs. SCE with the aid of Lewis acids that assisted in stabilising the catalyst's activity.^{7c} It was proposed that **1** was first reduced to $[\text{Fe}^0(\text{tpp})]^{2-}$, following which the metal centre attacks the electrophilic carbon of CO_2 to form an Fe(II) carbonyl complex. The presence of a Lewis acid (e.g. Mg^{2+}) forms an ion pair with the Fe(II)– CO_2 adduct, weakening the C–O bonds by drawing an electron pair from CO_2 to form $[(\text{tpp})\text{Fe}^{\text{II}}\text{CO}]$. Further steps in the catalytic cycle eventually release CO as a product and regenerate the catalyst.^{7b}

Figure 1. Structures of Fe porphyrin complex by Savéant and co-workers (**1**) and improved $[\text{Fe}(\text{tpp})]$ system by Constantin *et al.* (**2**)

Constantin *et al.* was able to further improve this system by modifying the phenyl rings with ionic groups. A water soluble catalyst was produced when four trimethylammonium groups were introduced at the para positions, which could efficiently convert CO_2 to CO in both DMF and aqueous electrolyte with only a small amount of H_2 produced as the reaction by-product.⁸ The addition of trimethylammonium groups in the ortho position of the four phenyl rings (**2**) drastically improved the catalytic ability with a decrease in overpotential (to 220 mV) and an increase in turn over frequency (TOF) of up to 10^6 s^{-1} . While the effect of the trimethylammonium groups is not fully understood, it is proposed that it was able to stabilise the Fe– CO_2 adduct via Coulombic stabilisation. This catalyst remains to date the most efficient homogeneous catalyst for CO production from CO_2 with Faradaic yields of close to 100%. There are a number of other

reported catalysts based on different transition metals that are efficient in other areas, but this work demonstrates how the product selectivity can be enhanced through modifying the catalyst's structure.

2.2.2 Organic Catalysts

Organic catalysts have also been studied on, although not as widely as the metal complexes. It is worthwhile to note that the organic systems for CO₂ reduction are much more favourable than the transition metals as they are less toxic and less expensive to synthesise. Courtemanche *et al.* reported work on a phosphane-borane organocatalyst that can reduce CO₂ in the presence of hydroboranes, HBR₂ (such as catecholborane where HBR₂ = HBcat) to form CH₃OBR₂ or (CH₃OBO)₃ that can be easily hydrolysed to methanol.⁹ The group managed to synthesise the organocatalyst, 1-Bcat-2-PPh₂-C₆H₄ (**3**) at 80% yield, and NMR spectroscopy studies showed that the reaction between HBcat and 1 mol% loading of 1-Bcat-2-PPh₂-C₆H₄ exclusively formed CH₃OBR₂ or (CH₃OBO)₃ in up to 99% yield, which translates to a high yield of methanol after hydrolysis of the compounds. The workers also reported that the catalytic system could achieve a high turnover number (TON) and turn over frequency (TOF) of >2950 and 853 h⁻¹ respectively, which indicated that the catalyst was highly efficient. It also exceeds the highest TOF value reported for CO₂ reduction to methanol of 495 h⁻¹, achieved by a homogeneous nickel catalyst.¹⁰ Current work is ongoing in order to fully understand the mechanism of the reaction, as well as to optimise the catalytic activity by focusing on the steric and electronic properties of the phosphorus and boron centres.

Figure 2. Structures of phosphane-borane organocatalyst by Courtemanche *et al.* (**3**) and 1,3-dimesitylimidazolium used by Gu and Zhang (**4**)

Gu and Zhang reported studies on N-Heterocyclic carbenes (NHC) that can function as organocatalysts to convert CO₂ to CO in the presence of aromatic aldehydes, being the first work done on organocatalysts that formed CO as the product.¹¹ Their work involved the use of cinnamaldehyde and 1,3-dimesitylimidazolium (**4**) which in the presence of CO₂ gives a carboxylic acid and CO gas, which was detected by gas chromatography analysis and through reduction of PdCl₂ solution. While they only reported on detecting the presence of CO gas, NHCs can be easily fine-tuned through changing the substituents on the N-atom so as to better optimise the catalytic efficiency. Their work also showed a ‘greener’ method to oxidize aromatic aldehydes under milder conditions using CO₂.

The studies from these two groups as well as findings in similar areas¹² have shown that organic catalysts have the potential in being efficient catalysts for CO₂ reduction. However, a limitation that is present is that most of the CO₂ reduction studies are performed under Schlenk line or glovebox conditions, thus indicating that the active catalyst is not stable under air or moisture conditions. Organic electrocatalysts on the other hand could help to overcome this issue, as CO₂ reduction studies carried out with electrocatalysts can be performed under atmospheric conditions. This would make it easier to utilise the catalysts on an industrial scale in future works. Vianello *et al.* reported in the early 1980s on the use of benzonitrile for CO₂ reduction where oxalate was selectively produced.¹³ However, the benzonitrile was reduced at a very negative potential of -2.28 V vs. SCE on a Pt sphere electrode in DMF solvent. Nevertheless, the information obtained at that time was surprising because it was thought that the radical anions formed from aromatic compounds would be carboxylated instead by CO₂ via electrophilic aromatic substitution.¹⁴

The next most intriguing yet controversial catalyst that has been widely explored on is the use of pyridine that can be relatively easily protonated to form pyridinium, which was first studied in the 1990s by Bocarsly and co-workers.¹⁵ It was reported that protonated pyridine (and other substituted protonated pyridine containing molecules) was able to facilitate the electrochemical reduction of CO₂ to methanol (MeOH) at -0.58 vs. SCE using a Pd electrode. The reported

Faradaic yield for MeOH was at only 30% due to the competing hydrogen evolution reaction. Further studies in this area have shown that the type of electrode material used with pyridiniums affected the type of products produced. Pt,¹⁶ Sn¹⁷ and Pt/C-TiO₂¹⁸ electrodes generated MeOH but glassy carbon,¹⁶ Au¹⁹ and polycrystalline Pt²⁰ electrodes showed no activity for CO₂ reduction. The many studies performed with pyridiniums to date have resulted in conflicting reports of the yields of the reduced CO₂ containing products, and many uncertainties remain with regards to the role that pyridinium plays in CO₂ reduction,²¹ but current efforts are still ongoing so as to better understand the reaction mechanism.²² Nevertheless, the pyridinium-based catalytic system represents a good example of how the electrode material and surface structure play an important role in CO₂ reduction. All of these various factors have to be taken into consideration in order to develop an efficient catalyst for CO₂ reduction.

2.3 Current Studies on Quinones

There have been several electrochemical studies carried out on quinones in order to examine their ability for electrocatalytic conversion of CO₂. One of the earlier studies was performed by Mizen and Wrighton, where they worked on 9,10-phenanthraquinone (PQ) and studied its electrochemical behaviour with CO₂ in acetonitrile (CH₃CN).²³ They demonstrated that the two-reduction peaks of quinones changes to a single reduction peak involving the transfer of two-electrons in the presence of CO₂. While they were unable to isolate the PQ-CO₂ adduct through electrochemical methods, they were able to isolate the PQ-CO₂ adduct via chemical means, as well as chemically synthesising the biscarbonate, PQ(CO₂)₂²⁻. The comparison of the UV-data showed that electrochemically reducing PQ in the presence of CO₂ does form the biscarbonate in solution. Their study has thus shown the ability of PQ for CO₂ uptake, and the reversibility of this uptake could serve as the basis for CO₂ sensing in non-aqueous media.

Further studies that involved quinones and CO₂ were carried to observe the ability of quinones for CO₂ capture. Studies were also conducted in various media such as ionic liquids (ILs),²⁴ aqueous²⁵ and organic solvents.²⁶ Gurken *et al.* reported on the different properties of various ILs and how the combination of ILs and CO₂ would affect the electrochemical reduction

of quinones.^{24a} Using naphthoquinone as their target quinone, they identified a suitable ionic liquid, 1-ethyl-3-methylimidazolium tricyanomethanide [emim][tcm] as the electrolyte for electrochemical separation. However their system had to overcome two major overpotentials. First was the ohmic overpotential arising from conduction limitations of ILs, and second was the concentration overpotential where the system had to overcome mass transfer limitations due to high viscosity of the solution.

Scovazzo *et al.* used 2,6-di-*tert*-butyl-1,4-benzoquinone (DtBBQ) to study its efficiency of separating CO₂ in an ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF₆].^{24b} Their method of separation was based on electrochemical pumping, which utilises a redox active molecule that can bind strongly to CO₂ in one of its redox states. By doing the reverse process (i.e. if CO₂ binds to the reduced state, the oxidised state will be formed in the reverse process), the binding constant of CO₂ will decrease, releasing the captured CO₂. Their study used the reduced form of DtBBQ, primarily DtBBQ²⁻, in the working compartment solution for the absorption of CO₂. Applying a positive potential to the working electrode oxidises DtBBQ²⁻ to DtBBQ, thereby releasing CO₂. Their work demonstrated that their system could selectively separate CO₂ at 1% levels (0.425 kPa) in a feed gas mixture of CO₂ and N₂, to produce pure CO₂ gas (85.3 kPa). However, DtBBQ and CO₂ had poor solubility in the ionic liquid, and the reduced form of DtBBQ was sensitive to oxygen, making the system less practical for use to separate CO₂ from the atmosphere. Nevertheless, their work has shown the quinone's potential for CO₂ separation, and further work could be done to resolve the oxygen sensitivity issue.

Yin *et al.* studied the use of various quinones on the electrochemical reduction of CO₂ in organic solvents and its implications on a Li-CO₂ battery where quinones could be of use for applications in energy storage systems.^{26b} In their study, apart from conducting electrochemical studies on the quinones, they also investigated how the addition of a Lewis acid such as Li⁺ would affect the reduction of quinones. The group found that quinones are capable of reducing CO₂ via an interaction between the reduced quinone and CO₂, and that Li⁺ forms strong interactions with quinone anions that would hinder quinone and CO₂ from interacting. While their work presented

various limitations for the development of a Li-CO₂ battery involving quinones, new ideas could be derived from the results that they have obtained.

2.4 Research Gap

In section 2.3, it is noted that most studies have shown the ability for quinones to capture CO₂, but relatively little work has been carried out to show if quinones are able to convert CO₂ into useful products. In this thesis, we aimed to better understand the mechanism of electrochemical reduction of CO₂ using various quinones via attempting to isolate and spectroscopically characterising the intermediates and products formed. In chapter 4, naphthoquinones were studied for their ability to function as electrocatalyst for CO₂ reduction while in chapter 5, anthraquinones were examined.

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Chapter 3

Experimental Methods

3.1 *Purchased Chemicals*

3.2 *Synthesis Procedures*

*3.2.1 Synthesis of tetra-*n*-butylammonium hexafluorophosphate*

3.2.2 Synthesis 2,3-dimethyl-1,4-naphthoquinone (DMNQ)

3.3 *Voltammetry*

3.4 *Controlled Potential Electrolysis Experiments*

3.5 *UV-Visible Spectroscopy*

3.6 *Nuclear Magnetic Resonance Spectroscopy*

3.7 *Reaction of $\text{NQ}(\text{CO}_2)_x^{2-}$ with CH_3I*

References

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3.1 Purchased Chemicals

The following chemicals were used as received : 1,4-naphthoquinone (NQ, Tokyo Chemical Industry Co., 98%), 2-methyl-1,4-naphthoquinone (MNQ, Sigma-Aldrich, 98%), 9,10-anthraquinone (AQ, Sigma-Aldrich, 97%), tetraethylammonium hexafluorophosphate (Et_4NPF_6 , Sigma-Aldrich, 99%), ferrocene (Fc, Sigma-Aldrich, 99%), hexafluorophosphoric acid (HPF_6 , Alfa Aesar, 60% w/w aqueous solution), tetra-*n*-butylammonium hydroxide ($n\text{Bu}_4\text{NOH}$, Alfa Aesar, 40% w/w aqueous solution), acetonitrile (CH_3CN , VWR Chemicals, HPLC grade), methanol (MeOH , Fulltime, HPLC grade), CO_2 (Air Liquide).

3.2 Synthesis Procedures

Tetra-*n*-butylammonium hexafluorophosphate ($n\text{Bu}_4\text{NPF}_6$)¹ and 2,3-dimethyl-1,4-naphthoquinone (DMNQ)² were synthesized in accordance with published procedures.

3.2.1 Synthesis of tetra-*n*-butylammonium hexafluorophosphate

The supporting electrolyte that was used in most of the electrochemical experiments was synthesized as follows : equal molar amounts of $n\text{Bu}_4\text{OH}$ and HPF_6 were reacted at room temperature (25 ± 2 °C). The precipitate was then washed with hot water until the washings had a $\text{pH} \geq 5$, and recrystallized from hot EtOH three times before drying under vacuum at 160 °C for 6 h. The white crystalline solids were subsequently stored under vacuum.¹

3.2.2 Synthesis of 2,3-dimethyl-1,4-naphthoquinone (DMNQ)

1,4-Naphthoquinone (1.08 g, 6.83 mmol), acetic acid (0.5 mL) and silver nitrate (0.64 g, 3.76 mmol) were dissolved in a solvent mixture of 20 mL of water and 40 mL of acetonitrile. Ammonium persulfate (1.90 g, 8.32 mmol) dissolved in 25 mL of water was added gradually to the stirred mixture for over 7.5 min. The mixture was incubated at 80 °C for 5 h and at room temperature overnight. 100 mL of water was added to the mixture that was then extracted twice with 25 mL of dichloromethane. The organic layer was washed twice with 50 mL of water, dried with sodium sulfate, filtered and concentrated under rotatory evaporation. The crude product

obtained was used to repeat the same experimental procedures to form yellow crystals (2.34 g, 56% yield). ^1H NMR (CDCl_3 , 300 MHz) δ 7.26 (s, 6H), 7.68 (m, 2H), 8.08 (m, 2H).²

3.3 Voltammetry

Cyclic Voltammetry (CV) and Square Wave Voltammetry (SWV) experiments were performed using a computer-controlled Eco Chemie Autolab PGSTAT302N potentiostat in a three electrode cell setup with a 1 mm diameter planar glassy carbon electrode (eDAO) working electrode, a platinum wire (Metrohm) auxiliary electrode, and a silver wire (eDAO) miniature reference electrode connected to the solution via a salt bridge containing 0.5 M $n\text{Bu}_4\text{NPF}_6$ in CH_3CN . The experiments were conducted within a Faraday cage located in a fumecupboard at room temperature (25 ± 2 °C) under argon or CO_2 . The electrochemical solutions were deoxygenated with argon for 5 mins prior to saturation with CO_2 gas. Unless otherwise stated, the CVs were recorded at a scan rate (v) of 0.1 V s^{-1} and SWVs were recorded with a pulse period (τ) of 25 Hz, step potential of 5 mV, and pulse amplitude of 20 mV. Ferrocene (Fc) was used as an internal standard where it was added to the test solution at the end of the experiment in order to obtain accurate potentials.

3.4 Controlled Potential Electrolysis Experiments

Controlled potential electrolysis (CPE) experiments were conducted in a two-compartment CPE cell separated by a sintered, no. 5 porosity ($1.0\text{-}1.7 \mu\text{m}$) glass frit. Hollow, cylindrical glassy carbon rods of identical size were used as the working and auxiliary electrodes. The electrodes were arranged symmetrically with respect to each other. The silver wire miniature reference electrode was connected to the test solution via salt bridge bridge containing 0.5 M $n\text{Bu}_4\text{NPF}_6$ in CH_3CN . Approximately 25 mL of solution was used in each compartment of the cell, and forced convection was achieved through bubbling of argon or CO_2 into the solution. The total number of electrons transferred during bulk electrolysis was calculated from equation 1:

$$n = \frac{Q}{NF} \quad (1)$$

Where n = number of electrons transferred per mole of the starting compound, Q = charge passed through (coloumbs), N = amount of the starting compound (moles), and F = Faraday's constant (96,485 C mol⁻¹).

3.5 UV-Visible Spectroscopy

UV-vis spectroscopy experiments were conducted with a PerkinElmer Model Lambda 750 spectrophotometer at 25±2 °C using an optically semi-transparent thin-layer electrochemical (OSTLE) cell with a path length of 0.5 mm. In-situ UV-Vis spectra were obtained by performing electrolysis in the OSTLE cell using a Pt mesh working electrode.³ The compound solution to be placed in the OSTLE cell was first deoxygenated using argon gas and the OSTLE cell was placed in a Schlenk tube and then filled with deoxygenated solution using a syringe. For UV-Vis spectra that was collected at low temperatures, a PerkinElmer flow cell connected to a Thermo Electron Neslab RTE 740 circulating bath containing propan-2-ol as the coolant was used to maintain low temperatures. To prevent condensation and maintain an oxygen free environment in the OSTLE cell, a high-volume flow of dry nitrogen gas was used to purge the cavity of the spectrometer. For studies in the presence of CO₂, the compound solution was saturated with CO₂ instead, and CO₂ was used to purge the cavity of the spectrometer.

3.6 Nuclear Magnetic Resonance Spectroscopy

Nuclear Magnetic Resonance (NMR) spectra were measured using a Bruker AV 300 spectrometer. For solvent suppression NMR, the NMR sample was prepared by adding 500 µL of the catholyte and 10% of CD₃CN (Cambridge Isotope Laboratories, Inc., 99.8 atom % D) into an NMR sample tube and was analysed by ¹H NMR spectroscopy to identify the presence of products. The peak of CH₃CN was suppressed by a solvent suppression sequence. The relaxation time of 16 sec between the pulses was used to allow for complete proton relaxation. The experiments were run for 16 scans and the reported spectrum are the average of two trials.

3.7 Reaction of $\text{NQ}(\text{CO}_2)_x^{2-}$ with CH_3I

$\text{NQ}(\text{CO}_2)_x^{2-}$ was electrochemically formed by a two-electron reduction of NQ (39.54 mg, 0.25 mmol) in the presence of CO_2 via CPE. The resulting solution in the working compartment of the electrochemical cell was transferred to a round-bottom flask containing CH_3I (1.87 mL, 0.03 mol) under nitrogen and stirred for 3 h at 25 ± 2 °C. The reaction mixture was then evaporated to dryness and Et_2O was added to dissolve the contents but not $n\text{Bu}_4\text{NPF}_6$. The solid electrolyte was filtered, and the resultant filtrate was evaporated to dryness. The filtrate was subsequently purified using preparative thin layer chromatography (Prep TLC) (25% ethyl acetate, 75% hexane) and flash column chromatography.

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Chapter 4

Naphthoquinones as CO₂ Electrocatalysts

4.1 Introduction

4.1.1 Solvent

4.1.2 Working Electrode

4.2 Electrochemical Behaviour of Naphthoquinones

4.2.1 Electrochemical Behaviour under Argon Conditions

4.2.2 Electrochemical Behaviour under CO₂ Conditions

4.3 Reduction of Naphthoquinones via CPE Experiments

4.3.1 CPE Reduction under Argon Conditions

4.3.2 CPE Reduction under CO₂ Conditions

4.4 UV-Visible Spectroscopy

4.4.1 Characterisation of Naphthoquinones

4.4.2 Ex-situ UV-Vis Spectroscopy

4.4.3 In-situ UV-Vis Spectroscopy

4.5 Attempted Isolation of $NQ(CO_2)_2^{2-}$ with CH_3I

4.6 Study of Products Formed via Proposed Catalytic System

4.7 Summary

References

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4.1 Introduction

Naturally occurring derivatives of naphthoquinones have been identified as functional molecules that are present in plants, bacteria and fungal species,¹ and they have been found to have important biological and pharmacological properties, such as Vitamin K₁ and K₂ which play an important role in regulating the blood-clotting response of the human body.² In structure, naphthoquinones are derived from naphthalene, with the addition of two carbonyl oxygen atoms, and the most stable and commonly reported being 1,4-naphthoquinone (NQ). The structural features of naphthoquinones allow them to undergo either a one- or two-electron reduction, and it is with this feature that allows it to participate in electron transfer processes, which is a property that is utilized in synthesizing anticancer drugs.³

This chapter aims to investigate the electrocatalytic ability of naphthoquinones for the reduction of CO₂ into more useful materials. Naphthoquinones were chosen in particular because they have good solubility in aprotic solvents, and the presence of an additional aromatic ring gives rise to ‘vacant sites’ which would allow for modifications to the quinones in order to fine tune their properties. For the following studies, acetonitrile (CH₃CN) solvent and the glassy carbon (GC) electrode were selected as the components of the experimental set-up to conduct the electrochemical study of the naphthoquinones.

4.1.1 Solvent

The solvents used in electrochemical studies are important because they determine the solubility of the analyte as well as the electrochemical window. It should also be able to dissolve the quinone and CO₂, together with its products formed and the electrolyte. Previous studies from group members have compared the electrochemical window of organic solvents such as dichloromethane (DCM), dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and acetonitrile (CH₃CN). It was found that CH₃CN has the largest potential window (from +2.4 V to -3.2 V *vs.* Fc/Fc⁺) and good CO₂ solubility, thus the bulk of the studies in this thesis were done using CH₃CN as the solvent.

4.1.2 Working Electrode

As described earlier, quinones exhibit an EE mechanism (two one-electron (E) steps), and the working electrode material was chosen based on the recorded electrochemical response. Studies have been performed comparing the electrochemical behaviour of quinones on Pt and GC, and unlike the voltammogram recorded on GC, the second reversible reduction process on Pt was affected by a slow heterogenous electron transfer.⁴ A more complicated electrochemical reaction occurs on the Pt electrode, which would hinder the study of the quinone-CO₂ interaction, hence Pt was not favoured. Furthermore, the hydrogen evolution reaction (HER) which is well documented on Pt electrodes even in aprotic solvents may interfere with CO₂ reduction.⁵ The HER would also give lower faradaic yields and reduce the efficiency of CO₂ trapping and conversion due to unwanted protonation reactions of the semiquinone and dianion forms. GC electrodes are known to be chemically stable and result in quinones exhibiting simpler voltammetric behaviour, thus the experiments were performed using the GC electrode.

4.2 Electrochemical Behaviour of Naphthoquinones

The three naphthoquinones studied were 1,4 naphthoquinone (NQ), 2-methyl-1,4-naphthoquinone (MNQ) and 2,3-dimethyl-1,4-naphthoquinone (DMNQ). Additional methyl groups on the aromatic ring alters the nucleophilicity of the quinone through inductive effects (Figure 1) but may also hinder the quinone and CO₂ from reacting. The effect of the quinone's nucleophilicity on CO₂ trapping together with its electrochemical behaviour were examined.

Figure 1. Quinones of interest arranged in increasing nucleophilicity (left to right)

4.2.1 Electrochemical Behaviour under Argon Conditions

Cyclic Voltammetry (CV) experiments were conducted to study the electrochemical behavior of NQ, MNQ and DMNQ under Ar conditions with the voltammograms shown in Figure 2 and with the results tabulated in Table 1.

Figure 2. CVs of 1mM DMNQ, MNQ and NQ/0.1 M $n\text{Bu}_4\text{NPF}_6$ in CH_3CN recorded at 0.1 V s^{-1} scan rate with a 1 mm diameter planar GC WE at $25 \pm 2^\circ \text{C}$ under Ar conditions.

Table 1. Redox potentials of NQ, MNQ and DMNQ with reference to Fc/Fc^+ . CV experiments were conducted with 0.1 M $n\text{Bu}_4\text{NPF}_6$ in CH_3CN with a 1 mm diameter planar GC WE at $25 \pm 2^\circ \text{C}$.

Quinone	$E_{\text{Q}/\text{Q}^{\cdot-}}^{\text{red}} / \text{V}$	$E_{\text{Q}/\text{Q}^{\cdot-}}^{\text{ox}} / \text{V}$	$ E_{\text{pp}}(\text{Q}/\text{Q}^{\cdot-}) / \text{mV}$	$E_{\text{Q}^{\cdot-}/\text{Q}_2^{\cdot-}}^{\text{red}} / \text{V}$	$E_{\text{Q}^{\cdot-}/\text{Q}_2^{\cdot-}}^{\text{ox}} / \text{V}$	$ E_{\text{pp}}(\text{Q}^{\cdot-}/\text{Q}_2^{\cdot-}) / \text{mV}$
NQ	-1.096	-1.028	68.4	-1.631	-1.560	70.8
MNQ	-1.174	-1.108	65.9	-1.670	-1.599	70.8
DMNQ	-1.269	-1.199	70.8	-1.775	-1.706	68.4

At first glance, it would seem that the quinones are able to delocalize the weak positive charge on the carbonyl carbon into the side ring and gain resonance stabilization, making them more Lewis basic. However, this would disrupt the aromaticity if the positive charge was delocalized into the side rings, possibly destabilizing the molecule instead. Thus, it is unlikely that the increase in basicity of the quinones occurs due to charge delocalization via resonance.

Nevertheless, the presence of electron-donating methyl groups increases the basicity of the quinones through the electron-donating inductive effect, but at the same time it reduces their electron affinities. Hence, the potentials are shifted towards more negative values, especially for DMNQ which has two methyl groups.

4.2.2 Electrochemical Behaviour under CO_2 Conditions

CV experiments were then conducted in the presence of CO_2 . Using NQ as an example, Figure 3 shows that NQ exhibits a single reduction peak corresponding to the transfer of two electrons per molecule of quinone when the CV was conducted in CH_3CN in the presence of CO_2 (red trace).

Figure 3. CVs of 1 mM NQ/0.1 M $n\text{Bu}_4\text{NPF}_6$ in CH_3CN under Ar (black trace) and CO_2 (red trace) at 0.1 V s^{-1} scan rate with a 1 mm diameter planar GC WE at $25 \pm 2 \text{ }^\circ\text{C}$.

Under CO_2 saturated conditions, a single reduction peak at $-1.10 \text{ V vs. Fc/Fc}^+$ was observed. This also corresponds to the potential of the first reduction reaction from Q to $\text{Q}^{\bullet-}$ for NQ under Ar conditions. This new reduction process was approximately twice the height of the first reactions observed under Ar (i.e. $i_p^{\text{red}(\text{CO}_2)} = 2 \times i_p^{\text{red}(1)}$), and equal to the sum of the respective peak currents ($i_p^{\text{red}(\text{CO}_2)} = i_p^{\text{red}(1)} + i_p^{\text{red}(2)}$). The second reduction peak at $-1.63 \text{ V vs. Fc/Fc}^+$ observed under Ar conditions was also absent under CO_2 conditions, and this can be explained by

the reaction between $Q^{\bullet-}$ and CO_2 , as well as the higher electron affinity of the product $Q(CO_2)_x^{\bullet-}$ (where $x = 1$ or 2) due to the electron-withdrawing inductive effect from the additional carbonyl groups. Thus the reduction process of $Q(CO_2)_x^{\bullet-}$ to $Q(CO_2)_x^{2-}$ occurs at a similar potential of the reduction of Q to $Q^{\bullet-}$. It should also be noted that the reduction potentials of quinones are known to be highly sensitive to hydrogen bonding interactions, where both reduction peaks would shift to less negative potentials with stronger or more extensive hydrogen bonding. It is thus possible for the quinone to interact with CO_2 and result in the merger of the two reduction peaks given that CO_2 is a stronger electrophile than traditional hydrogen donors like water or alcohols.

From the voltammograms, it is proposed that an initial ECE mechanism is likely to occur when NQ is in the presence of excess CO_2 . $Q^{\bullet-}$ first reacts with either one or two molecules of CO_2 , then another reduction process occurs and the carboxylated dianion $Q(CO_2)^{2-}$ may capture another molecule of CO_2 to form the bis(carboxylate) dianion $Q(CO_2)_2^{2-}$ due to the increase in basicity. In this case, the overall final mechanism will be an ECEC mechanism as shown in Scheme 1.

Scheme 1. ECEC mechanism of NQ in the presence of CO_2

Figure 4 shows the CV experiments conducted at varying scan rates (from 0.1 V s^{-1} to 1.0 V s^{-1}) in the presence of CO_2 for the three quinones to compare their electrochemical behavior. With increasing scan rates, the time taken for each CV experiment decreases. If the scan rate is fast enough to outrun the reaction kinetics between two species, in this case between the reduced quinone and CO_2 , a noticeable change would be observed in the voltammograms and it can be used to deduce the overall reaction mechanism. This makes CV a useful method in studying the

kinetics of a chemical reaction. For instance, if the scan rate is fast enough to overcome the chemical reaction between $Q^{\bullet-}$ and CO_2 , the reaction would then follow an EEC mechanism instead. At even higher scan rates where all chemical reactions are outrun, an EE mechanism would be expected to be observed.

Figure 4. CVs of 1mM NQ, MNQ and DMNQ/0.1 M nBu_4NPF_6 in CH_3CN under CO_2 conditions at various scan rates with a 1mm diameter planar GC WE at 25 ± 2 °C. Voltammograms indicated by the dashed trace represent those performed in deoxygenated solution, prior to saturation with CO_2 . The data was normalized by dividing the currents by $v^{0.5}$ where v = scan rate

All three quinones have the characteristic single reduction peak under CO_2 conditions, with NQ reduced at -1.10 V vs. Fc/Fc^+ , MNQ at -1.15 V vs. Fc/Fc^+ and DMNQ at -1.25 V vs. Fc/Fc^+ in Figure 4. It is observed that at higher scan rates, the reduction potential for NQ seems to be shifting towards more negative potentials and the reduction peak appears to be splitting, but for MNQ and DMNQ, no splitting is observed. It is possible that the chemical reaction between the NQ dianion and CO_2 is relatively slower compared to MNQ and DMNQ because of

nucleophilicity differences, thus the increase in scan rates could overcome the chemical step of NQ and CO₂. It is also noted that the shifting to larger potentials with faster scan rate could be due to the uncompensated solution resistance as well as limitations in the heterogeneous electron transfer kinetics. For NQ, the absence of electron-donating methyl substituents reduces its nucleophilicity, making it less likely to attack CO₂ and form the dicarboxylate anion thus having slower reaction kinetics. On the other hand, MNQ and DMNQ have electron-donating methyl substituents that increases the electron density of the quinone. This increase in electron density could make it more likely for MNQ and DMNQ to attack CO₂, thus faster scan rates were unable to overcome the chemical reaction between reduced quinone and CO₂. It is also possible that the observations as seen from the CVs could be arising from strong interactions between reduced quinone and CO₂ instead, such as that seen in the case of hydrogen bonding between quinone and H₂O, which cannot be overcome at fast scan rates. In summary, the reduction of NQ requires less energy but MNQ and DMNQ show higher nucleophilicity due to its electron-donating methyl substituents. More experiments were conducted in order to investigate which of the quinones would be most suitable as an electrocatalyst for CO₂ capture and conversion.

4.3 Reduction of Naphthoquinones via CPE Experiments

Stepwise controlled potential electrolysis (CPE) experiments were conducted to reduce NQ, MNQ and DMNQ to their semiquinone and dianionic states under Ar and CO₂ conditions in CH₃CN in order to study the stability of the reduced species within the timescale of the experiments ($t \sim$ mins to hours).

4.3.1 CPE Reduction under Argon Conditions

The CVs before and after CPE experiments were recorded, as shown in Figure 5 for NQ, Figure 6 for MNQ and Figure 7 for DMNQ.

Figure 5. CVs of 1 mM NQ/0.1 M $n\text{Bu}_4\text{NPF}_6$ in CH_3CN recorded at 0.1 V s^{-1} scan rate with a 1 mm diameter planar GC WE at $25 \pm 2^\circ \text{C}$ at various times during electrolysis under Ar conditions.

The CPE experiments under an Ar atmosphere show that NQ undergoes a one-electron reduction to form the semiquinone first, followed by a second electron transfer to form the dianion species at more negative potentials. NQ and its reduced species display the typical quinone behavior as shown in Figure 5. It is noted that the CV profile is shifted towards more positive current direction after the first electron reduction, while the CV profile shifts by a greater extent after the second electron reduction. This observation occurs as the CV starting potential is at $+0.5 \text{ V}$, which is much more positive than the first reduction potential of NQ. Any reduced species that is near the WE surface would be oxidized back to the neutral quinone, giving rise to a positive current and so results in the positive shift of the CV profile. The same reasoning can be applied for the CVs of the one- and two- electron oxidation CPE. Through the CPE experiments, it is found that both the semiquinone and dianion species were stable under the timescale of the experiment ($t \sim 30 \text{ mins}$), and NQ can be reversibly converted between its neutral, semiquinone and dianionic states.

Figure 6. CVs of 1 mM MNQ/0.1 M $n\text{Bu}_4\text{NPF}_6$ in CH_3CN recorded at 0.1 V s^{-1} scan rate with a 1 mm diameter planar GC WE at $25 \pm 2^\circ \text{C}$ at various times during electrolysis under Ar conditions.

Figure 7. CVs of 1 mM DMNQ/0.1 M $n\text{Bu}_4\text{NPF}_6$ in CH_3CN recorded at 0.1 V s^{-1} scan rate with a 1 mm diameter planar GC WE at $25 \pm 2^\circ \text{C}$ at various times during electrolysis under Ar conditions.

In the case of MNQ and DMNQ, both quinones did not display the same chemical reversibility as observed with NQ. The neutral species were not regenerated after re-oxidation, suggesting that the semiquinone and dianion species of both quinones were not stable under the timescale of the CPE experiments ($t \sim 30$ mins). Since both MNQ and DMNQ contain electron-

donating methyl substituents which increases the nucleophilicity of the quinones, its semiquinone and dianion forms may be highly reactive. Thus, it is likely that the semiquinone and dianionic species may have undergone side reactions with either the solvent, trace water or trace impurities, compromising the chemical reversibility of the quinones.

The electrolyte used in the CPE experiments was $n\text{Bu}_4\text{NPF}_6$ and it serves to minimize the effects of migration as well as reduce resistance in the cell. By using an electrolyte with less bulky cations, it may allow for better interactions with the semiquinone and dianionic species. Therefore, a similar CPE experiment was conducted with DMNQ, which has more methyl substituents, in 0.1 M of Et_4NPF_6 instead and the CVs that were recorded are shown in Figure 8.

Figure 8. CVs of 1 mM DMNQ/0.1 M Et_4NPF_6 in CH_3CN recorded at 0.1 V s^{-1} scan rate with a 1 mm diameter planar GC WE at $25 \pm 2^\circ \text{C}$ at various times during electrolysis under Ar conditions.

Comparing the two CV profiles of differing electrolyte conditions of bulk electrolysis, DMNQ seems to show similar behavior despite a change in the electrolyte used. The smaller electrolyte cation was unable to aid in stabilizing the semiquinone and dianion species. Thus it can be concluded that the semiquinone and dianion species of DMNQ were too reactive and unstable. Attempts to perform the experiment with smaller cations like Me_4NPF_6 and LiClO_4 were not possible. Me_4NPF_6 is insoluble in CH_3CN while Li^+ ions will form strong interactions with the

reduced quinone forms and precipitate on the surface of the electrode, which causes a distortion on the voltammograms.

4.3.2 CPE Reduction under CO_2 Conditions

The electrochemical behavior of NQ, MNQ and DMNQ as well as their respective reduced species were then investigated in the presence of CO_2 . Figure 9 shows the CVs recorded before and after the CPE experiment.

Figure 9. CVs of 1 mM a) NQ, b) MNQ and c) DMNQ/0.1 M $n\text{Bu}_4\text{NPF}_6$ in CO_2 -saturated CH_3CN recorded at 0.1 V s^{-1} scan rate with a 1 mm diameter planar GC WE at $25 \pm 2^\circ \text{C}$ before and after electrolysis.

From the CV profiles, all three quinones were able to undergo a two-electron reduction reaction, and the reduced species were stable under the time scale of the experiment. In the presence of Ar, the semiquinone and dianion species of MNQ and DMNQ were shown to be unstable. When the experiment was conducted in the presence of CO₂ instead, the reduced species of MNQ and DMNQ appeared to be long-lived. The presence of CO₂ apparently exerts a stabilizing effect on the reduced species, presumably via a chemical reaction. It is likely that the negatively charged oxygen atoms of the reduced quinone species are strongly interacting with the electropositive carbon centre of CO₂ (as shown in Scheme 1). After the two electron CPE reduction, the solution containing the reduced quinone species was then purged with Ar and the electrochemical behavior of NQ, MNQ and DMNQ were recorded in the CVs shown in Figures 10, 11a) and 11b) respectively.

Figure 10. CVs of 1 mM NQ/0.1 M *n*Bu₄NPF₆ in CO₂-saturated CH₃CN recorded at 0.1 V s⁻¹ scan rate with a 1 mm diameter planar GC WE at 25±2 °C. Solid trace : CV measured after two electron reduction electrolysis, dashed trace : CV measured after reduced solution was purged with Ar for 30 minutes.

After purging the reduced solution with Ar to remove excess CO₂, the electrochemical behavior of NQ was noted to be different compared to its typical behaviour, with an extra peak detected at more negative potentials (at approximately -1.4 V vs. Ag) (Figure 10). Nevertheless, it

appears that purging the solution with Ar at least partly regenerates the cyclic voltammetric response expected for the reduced quinone. From this observation, it can be concluded that the complexation between the reduced quinone and CO_2 is relatively weak, such that purging with Ar is able to ‘break’ the complex that forms and regenerates the reduced quinone. It is also possible that in the dianionic state, NQ^{2-} is able to react with CO_2 to form some reaction product that is detected at more negative potentials (-1.4 V vs. Ag).

Figure 11. CVs of 1 mM a) MNQ and b) DMNQ/0.1 M $n\text{Bu}_4\text{NPF}_6$ in CO_2 -saturated CH_3CN recorded at 0.1 V s^{-1} scan rate with a 1 mm diameter planar GC WE at $25 \pm 2^\circ \text{C}$. Solid trace : CV measured after two electron reduction electrolysis, dashed trace : CV measured after reduced solution was purged with Ar for 30 minutes.

Similarly, the solutions for MNQ and DMNQ after CPE reduction was also purged with Ar for 30 mins. The typical quinone behavior was regenerated for both quinones, indicating that the reduced complexes of the dianions of MNQ and DMNQ with CO_2 [$\text{Q}(\text{CO})_2^{2-}$] were able to be fully converted back into the quinone dianions (Figure 11). Among the three quinones, DMNQ contains two electron-donating methyl groups, making it the most nucleophilic and expected to be the most reactive towards CO_2 . It appears that the semiquinone and dianion species of DMNQ were stabilized through interactions with CO_2 , but unable to irreversibly react with CO_2 during bulk electrolysis. The presence of the methyl substituents could have resulted in steric hinderance, which prevents DMNQ from irreversibly *reacting* with CO_2 but not restricting the two species from weakly *interacting*. MNQ, which has only one methyl substituent, would appear to be less sterically hindered than DMNQ, thus expected to be more likely to react with CO_2 compared to DMNQ. However, the CV profiles after purging with Ar show that MNQ was also unable to

irreversibly react with CO₂. The presence of just one methyl substituent does not appear to significantly increase the nucleophilicity of the quinone and instead brings about great steric hindrance to prevent the quinone from reacting with CO₂. This result was unexpected because accessibility to the other oxygen atom is unaffected by the additional methyl substituent.

In the proposed mechanism, each quinone molecule should ideally capture and convert two CO₂ molecules. Being more nucleophilic than NQ, MNQ and DMNQ should be more reactive towards CO₂ and thus work as a suitable electrocatalyst for CO₂. However, the methyl substituents appear to sterically hinder the oxygen atoms on the quinone from reacting with CO₂. Although NQ is the least nucleophilic among the three quinones, it is the least sterically hindered and also has a lower reduction potential, thus a lower amount of energy would be consumed.

From this experiment, it appears that the reaction of the quinone and CO₂ can be distinguished by two pathways. The first is that quinones are able to undergo a weak interaction with CO₂ to form the Q(CO)₂²⁻ intermediate species. This pathway can be observed occurring in the three quinones, NQ, MNQ and DMNQ, where the CVs measured under CO₂ conditions is significantly different to that measured under Ar conditions, indicating that an interaction is present. Due to the weak interactions, the intermediate species is extremely difficult to isolate from solution as a stable solid compound. Nevertheless, the presence of this interaction is still interesting as it results in a large lowering of the reduction potential, which translate to lower energy consumption. The second reaction pathway occurs if a suitable quinone is selected, upon forming the Q(CO₂)₂²⁻ species, the quinone can act as a catalyst to facilitate the reduction of CO₂ to form useful products. By having the CO₂ bind to the reduced quinone, it could perhaps make it more favourable for the CO₂ to react with the trace water present in the solvent to obtain a proton source in order to form other products. The exact mechanism on how CO₂ is converted to other possible protonated products after the formation of Q(CO)₂²⁻ was not explored in this thesis, but an attempt was made to test and identify the products that are formed, and the results will be discussed in section 4.6.

4.4 UV-Visible Spectroscopy

Most quinones in their neutral or reduced forms are coloured compounds and absorb light in the UV-visible region of the electromagnetic spectrum. Thus, UV-Visible spectroscopy was utilized to characterize the neutral quinones in the absence and presence of CO_2 , as well to ascertain the formation of intermediates found in the CO_2 mechanism.

4.4.1 Characterisation of Naphthoquinones

Figures 12 and 13 show the UV-vis spectra of the neutral quinones NQ, MNQ and DMNQ in the absence and presence of CO_2 , with their absorption wavelengths presented in Table 2.

Figure 12. UV-vis spectra of 0.2 mM NQ, MNQ and DMNQ/0.1 M $n\text{Bu}_4\text{NPF}_6$ in CH_3CN in the absence of CO_2 , using a cell with path length 0.5 mm.

Figure 13. UV-vis spectra of 0.2 mM NQ, MNQ and DMNQ/0.1 M $n\text{Bu}_4\text{NPF}_6$ in CO_2 -saturated CH_3CN , using a cell with path length 0.5 mm.

Table 2. Absorption wavelengths of NQ, MNQ and DMNQ in the absence and presence of CO_2 .

Absence of CO_2				Presence of CO_2		
Quinone	NQ	MNQ	DMNQ	NQ	MNQ	DMNQ
Absorption maxima / nm	194	193	195	194	194	193
	249	250	244	249	250	245
	332	331	262	332	331	262
			328			329

Comparing the absorption wavelengths in the absence and presence of CO_2 , NQ, MNQ and DMNQ are unaffected by the presence of CO_2 , indicating that there was a negligible reaction, if any, between the neutral quinones and CO_2 . Therefore the quinone has to be reduced to either its semiquinone or dianion forms before a reaction can occur between CO_2 and the quinones. Together with the data obtained from the CPE experiments, NQ seems to be the most reactive quinone in its reduced states (since extra voltammetric peaks were observed at the end of the

electrolysis). Therefore, NQ has been selected as the focus for the following studies in this chapter.

4.4.2 *Ex-Situ UV-Vis Spectroscopy*

Ex-situ UV-vis spectroscopy was first performed in order to obtain the spectrums for the semiquinone and dianion species so as to determine the intermediates formed in the CO₂ mechanism, as well as to study the stability of the intermediates. Ex-situ UV-vis spectroscopy was carried out by doing CPE reduction of the quinone using the electrolysis cell, and then transferring the solution into the OSTLE cell before measurements were taken at 30 mins interval over a period of 24 hours. The UV-vis spectra of the semiquinone and dianion were first taken under Ar conditions, as shown in Figure 14.

Figure 14. UV-vis spectra obtained of 0.2 mM NQ/0.1 M $n\text{Bu}_4\text{NPF}_6$ in CH_3CN under Ar conditions after a) two electron and b) one electron reduction over a period of 24 hours at 25 ± 2 °C. First UV-vis scan (red) was taken immediately, followed by spectrum plots at every 5-hour interval.

Comparing Figures 14a) and 14b), it appears that the semiquinone and dianion species seem to have undergone side reactions during the transfer of solution into the OSTLE cell before the UV-vis measurements of the species could be taken. Decay of the semiquinone and dianion species back to neutral NQ is also possible, however even after a period of 24 hours, the spectrum obtained after reduction of NQ did not resemble the spectrum of neutral NQ. Thus it is likely that the semiquinone and dianion species generated are highly reactive and they rapidly undergo side reactions upon the slightest exposure to air.

Figure 15. UV-vis spectra of 0.2 mM a) NQ^{•-} and b) NQ^{2•-}/0.1 M *n*Bu₄NPF₆ in CH₃CN under CO₂ conditions over a period of 24 hours at 25±2 °C. First UV-vis scan (red) was taken immediately, followed by spectrum plots at every 5-hour interval.

The same experiment was repeated but in the presence of CO₂, and Figures 15a) and 15b) show the spectra of the semiquinone and dianion under CO₂ conditions. For both spectrums, appearance of new peaks with absorption maxima at 208 and 245 nm was observed, and there was an increase in the absorbance for the shoulder at around 335 nm. This shows that there is a formation of a new species during bulk electrolysis, most likely NQ(CO₂)₂^{2•-}, and NQ(CO₂)₂^{2•-} is also stable over a period of 24 hours with a slow decay back to the neutral quinone.

Measurement of the spectrum of NQ(CO₂)^{•-} (i.e. intermediate formed as a result of the reaction of NQ^{•-} and CO₂) was attempted by holding the potential at a slight negative over $E_{Q/Q\cdot-}$

until an equivalent of one electron has passed. This was however not achieved because any $\text{NQ}(\text{CO}_2)^{\bullet-}$ present at the electrode surface would be instantaneously reduced to $\text{NQ}(\text{CO}_2)_2^{2-}$ as a result of the closeness in the values of $E_{\text{Q}^{\bullet-}/\text{Q}_2^-}$ and $E_{\text{Q}/\text{Q}^{\bullet-}}$, which indicates that $\text{NQ}(\text{CO}_2)^{\bullet-}$ has a greater electron affinity than $\text{NQ}^{\bullet-}$. It was thus not possible to obtain a bulk solution of $\text{NQ}(\text{CO}_2)^{\bullet-}$ only. It should be noted that the spectra of $\text{NQ}(\text{CO}_2)^{\bullet-}$ and $\text{NQ}(\text{CO}_2)_2^{2-}$ obtained via ex-situ UV-Vis spectroscopy are therefore highly similar.

4.4.3 In-Situ UV-Vis Spectroscopy

In order to further investigate the intermediates formed under Ar and CO_2 conditions, in-situ electrochemical UV-vis spectroscopy experiments were conducted on NQ to attempt to generate the spectrum for $\text{NQ}^{\bullet-}$, NQ^{2-} and $\text{NQ}(\text{CO}_2)^{\bullet-}$.

Figure 16. In-situ UV-vis spectra obtained during the reduction of 0.2 mM NQ/0.1 M $n\text{Bu}_4\text{NPF}_6$ in CH_3CN under Ar conditions at -25°C .

From the spectrum shown in Figure 16, two changes can be observed occurring as the potential applied for CPE reduction increases by -0.1 V under Ar conditions, and these changes presumably would correspond to the formation of $\text{NQ}^{\bullet-}$ and NQ^{2-} . The first change in the

spectrum occurs when a potential of -1.0 V *vs.* Ag is applied. There is a decrease in absorption loss of NQ at 194 and 250 nm, and formation of new absorption peaks occurs at 208 and 304 nm. An appearance of a shoulder at 268 nm is also observed. As the applied potential increases, no major changes in the spectrum occurs until the applied potential reaches -1.4 V *vs.* Ag. The peak at 208 nm shifts to form a new peak at 213 nm, and the peak at 304 nm is no longer present. The shoulder at 268 nm also shifts and forms a new peak at 270 nm. Further increase of the applied potential to -2.0 V *vs.* Ag did not show any changes to the overall shape of the spectrum, which indicates that there is no further reduction of the compound. From the in-situ electrochemical data obtained, it can be deduced that the spectrum collected at -1.0 V *vs.* Ag corresponds to $\text{NQ}^{\bullet-}$, and the spectrum at -1.4 V *vs.* Ag corresponds to NQ^{2-} . Oxidation of the dianion back to the neutral quinone was attempted, but the neutral quinone was unable to be regenerated, suggesting that NQ^{2-} is highly reactive and may have undergone side reactions upon its formation in solution.

Figure 17. In-situ UV-vis spectra obtained during the a) reduction and b) reverse oxidation of 0.2 mM NQ/0.1 M $n\text{Bu}_4\text{NPF}_6$ in CH_3CN under CO_2 conditions at 25 ± 2 °C.

The in-situ electrochemical experiments were then performed in the presence of CO_2 . Changes in the spectrum could be observed during the CPE reduction in Figure 17a), which also could presumably correspond to $\text{NQ}(\text{CO}_2)^{\bullet-}$ and $\text{NQ}(\text{CO}_2)^{2-}$. The changes in the spectrum occur fairly quickly when a potential of -0.8 V vs. Ag is applied. In the first UV-vis scan at -0.8 V vs. Ag, the absorbance of the peak at 194 nm decreases, with the appearance of a new absorption peak at 211 nm. The absorption peak at 252 nm of NQ also shifts to form a new peak at 249 nm. Following the second UV-vis scan at -0.8 V vs. Ag, the absorbance peak at 199 nm is lost, and there is an increase in the absorbance of the peak at 211 nm. The shoulder at 340 nm increases in absorbance as well. The applied potential was increased by intervals of 0.1 V until -1.6 V vs. Ag,

and no changes in the spectrum was observed. The new peaks formed at 211 and 249 nm is relatively close to the absorption values obtained from the ex-situ UV-vis of $\text{NQ}(\text{CO}_2)^{2-}$. Oxidation of $\text{NQ}(\text{CO}_2)^{2-}$ back to the neutral quinone was also possible, as a change in the spectrum was observed at -0.8 V vs. Ag from Figure 17b). The absorbance of the peak at 211 nm decreases, and a small absorption band can be seen forming at 200 nm. Further decrease in the applied potential regenerates the neutral quinone, as the spectrum corresponds to the neutral quinone. The reversibility of the reactions further indicates that CO_2 is able to stabilize the dianion species, allowing NQ to be reversibly reduced within the timescale of the experiments ($t \sim 1$ hour)

Through the in-situ data under CO_2 conditions, the reduction spectrum of the first scan at -0.8 V vs. Ag shows the transition between the neutral quinone and $\text{NQ}(\text{CO}_2)^{2-}$. The spectrum could possibly be of $\text{NQ}(\text{CO}_2)^{\bullet-}$, since the reduction of $E_{\text{Q}/\text{Q}^{\bullet-}}$ and $E_{\text{Q}^{\bullet-}/\text{Q}^{2-}}$ under CO_2 conditions occurs at the same potential. However it is difficult to confirm that the spectrum corresponds to $\text{NQ}(\text{CO}_2)^{\bullet-}$ since it is hard to isolate the intermediate during the reduction process. It is also noted that the in-situ electrochemical experiments were performed using a Pt mesh, thus the electrochemical behavior of the quinones differ from that on GC. Nevertheless, comparing the data obtained from the in-situ and ex-situ UV-vis experiments, the spectrum from the CO_2 experiments appear to be the same, indicating that the product obtained from the second reduction reaction using Pt and GC are be similar. The spectrums of $\text{NQ}^{\bullet-}$ and NQ^{2-} differ from $\text{NQ}(\text{CO}_2)^{\bullet-}$ and $\text{NQ}(\text{CO}_2)^{2-}$ as well, which confirms that the presence of CO_2 produces different intermediates compared to the quinone under Ar conditions.

4.5 Attempted Isolation of $\text{NQ}(\text{CO}_2)_2^{2-}$ with CH_3I

Attempts were made to isolate $\text{NQ}(\text{CO}_2)_2^{2-}$ by reacting it with CH_3I , an electrophile that is an excellent methylating agent with iodide as a good leaving group. Scheme 2 shows the proposed reaction pathway that would occur between $\text{NQ}(\text{CO}_2)_2^{2-}$ and CH_3I . NQ was reacted with CH_3I that was 120 times in excess, as trace water present in the solvent can hydrogen bond to the quinone and provide kinetic stabilisation, preventing the desired reaction from occurring. The amount of trace water typically present in the solvent is approximately 50 mM (1.25 mmol).⁴ **1a** was the

expected product of the reaction between $\text{NQ}(\text{CO}_2)_2^{2-}$ and CH_3I , however only the neutral quinone was obtained after purification of the reaction.

Scheme 2. Proposed reaction pathways for the isolation of $\text{NQ}(\text{CO}_2)_2^{2-}$ with CH_3I .

4.6 Study of Products Formed via Proposed Catalytic System

With the preliminary CPE data and UV-visible spectroscopy data obtained, the catalytic system of NQ and CO_2 was further investigated by attempting to test for CO_2 reduction products that were formed during the reaction mechanism. The electrochemical behavior of the reduced species of NQ in CO_2 -saturated CH_3CN was studied in a CPE experiment, and its CV behavior was plotted in Figure 18.

Figure 18. CVs of 1 mM NQ/0.1 M $n\text{Bu}_4\text{NPF}_6$ in CO_2 -saturated CH_3CN recorded at 0.1 V s^{-1} scan rate with a 1 mm diameter planar GC WE at $25 \pm 2^\circ\text{C}$ at various times during electrolysis.

NQ undergoes a two-electron reduction in the presence of CO₂, which is similar to the behavior obtained for NQ under Ar conditions. Its reduced form can also be oxidized back to the neutral quinone, thus the semiquinone and dianion forms can be considered to be stable under the timescale of the CPE experiments ($t \sim$ mins). Extensive purging of the solution ($\sim$ 15mins) with Ar after the reverse CPE oxidation generates the standard quinone behavior (Figure 19), indicating that the reaction between NQ and CO₂ only occurs after reduction of the quinone and not with its neutral form. Nevertheless, it is likely that the neutral NQ is interacting with several CO₂ molecules in a manner similar to hydrogen bonding (ie the oxygen atom of the quinone and the carbon atom of CO₂ interact via electrostatic interactions). An intriguing observation is the shift of E_{Q1} and E_{Q2} towards less negative potentials after purging with Ar at the end of the CPE experiments. This suggests that a compound, probably a hydrogen donor, was formed through the reduction and oxidation cycle and it exerts a noticeable influence on the reduction of NQ. The shift in E_{Q2} is much greater than the shift of E_{Q1}, which is similar to the behavior that was previously seen with hydrogen donors.⁶ It is also possible that the shifts were caused by absorption of water from the atmosphere into the solution. However, a significant amount of water will be needed to give rise to the magnitude of the shifts observed in Figure 19.

Figure 19. CVs of 1 mM NQ/0.1 M $n\text{Bu}_4\text{NPF}_6$ in CH_3CN recorded at 0.1 V s^{-1} scan rate with a 1 mm diameter planar GC WE at $25 \pm 2^\circ \text{C}$. Solid trace : CV measured before electrolysis, dashed trace : CV measured after reduced solution undergoes reverse CPE oxidation and purged with Ar for 15 minutes.

Previous work in the field of electrochemical CO_2 reduction have reported the formation of formic acid,⁷ oxalic acid⁸, methanol⁹ and ethanol¹⁰ which are capable of interacting with the quinone via hydrogen bonding. Tessensohn et al. have established a method of measuring the hydrogen donor strength in aprotic solvents by using the voltammetric behaviour of quinones via the potential separation between the two one-electron processes, i.e. $\Delta E^{\text{red}} = |E_{\text{Q1}} - E_{\text{Q2}}|$, which is inversely related to the strength of the interactions.^{6a} It is thus suspected that a hydrogen donor (i.e. weak carboxylic acid or alcohol) was produced during the reduction and oxidation cycle of NQ in the presence of CO_2 . A strong carboxylic acid is unlikely to be produced as the standard two one-electron reduction behaviour of the quinone would not be observed; the presence of a strong carboxylic acid would result in a single two-electron reduction occurring at more positive potentials with slow electron transfer kinetics and poor chemical reversibility.

To support the claim of the presence of a hydrogen donor, continuous CV cycling of up to 100 cycles was performed in the absence and presence of CO_2 . After the CV cycles, the solution

was then purged with Ar to remove CO₂, and the CV profiles after purging were plotted, as shown in Figure 20.

Figure 20. CVs of 1 mM NQ/0.1 M Et₄NPF₆ in CH₃CN recorded at 0.1 V s⁻¹ scan rate with a 1 mm diameter planar GC WE at 25±2 °C. (Solid trace: 1st scan, dashed trace: 100th scan)

Table 3. Measured absolute potentials (vs. reference electrode) with 0.1 M Et₄NPF₆ in CH₃CN with a 1 mm diameter planar GC WE at 25±2 °C.

	Control (Absence of CO ₂)				After CO ₂ Removal			
	E_{Q1} / mV	E_{Q2} / mV	ΔE^{red} / mV	ΔE^{red} (1 st -100 th) / mV	E_{Q1} / mV	E_{Q2} / mV	ΔE^{red} / mV	ΔE^{red} (1 st -100 th) / mV
1 st Scan	-803.22	-1333.00	529.78	31.78	-798.80	-1343.20	544.40	148.88
100 th Scan	-795.90	-1293.90	498.00		-762.18	-1157.70	395.53	

Comparisons were made between the experiments performed in the absence (control) and the presence of CO₂ (after CO₂ removal). The ΔE^{red} obtained for the control experiment was 529.78 mV for the 1st scan, and 498.00 mV for the 100th scan, with a difference of 31.78 mV. On the other hand in the presence of CO₂, the ΔE^{red} of the 1st scan is 544.40 mV and 395.52 mV for the 100th scan (i.e. the 100th scan refers to the CV after purging with Ar upon completion of the 100th scan) with a difference of 148.88 mV (~ five times larger than the control). The slight increase in current observed is likely due to the increase in concentration of the quinone from the loss of solvent during purging.

By repeating the above experiment at a faster scan rate, the ΔE^{red} between the start and the end of the CV should be smaller under CO_2 conditions since lesser time is allowed for the quinones to react with CO_2 and form the product. Thus faster scan rates of 0.4 and 1.0 V s^{-1} were applied and the CVs are shown in Figures 20 and 21 with their absolute potentials tabulated in Table 4.

Figure 20. CVs of 1 mM NQ/0.1 M Et_4NPF_6 in CH_3CN recorded at 0.4 V s^{-1} scan rate with a 1 mm diameter planar GC WE at $25 \pm 2^\circ \text{C}$. (Solid trace: 1st scan, dashed trace: 100th scan)

Figure 21. CVs of 1 mM NQ/0.1 M Et_4NPF_6 in CH_3CN recorded at 1.0 V s^{-1} scan rate with a 1 mm diameter planar GC WE at $25 \pm 2^\circ \text{C}$. (Solid trace: 1st scan; dashed trace: 100th scan)

Table 4. Measured absolute potentials (vs. reference electrode) with 0.1 M Et₄NPF₆ in CH₃CN with a 1 mm diameter planar GC WE at 25±2 °C.

	Control (Absence of CO ₂)				After CO ₂ Removal			
	0.4 V s ⁻¹		1.0 V s ⁻¹		0.4 V s ⁻¹		1.0 V s ⁻¹	
	ΔE^{red} / mV	ΔE^{red} (1 st -100 th) / mV	ΔE^{red} / mV	ΔE^{red} (1 st -100 th) / mV	ΔE^{red} / mV	ΔE^{red} (1 st -100 th) / mV	ΔE^{red} / mV	ΔE^{red} (1 st -100 th) / mV
1 st scan	542.19	2.9	554.46	-0.02	545.09	121.81	568.58	91.24
100 th scan	539.29		554.48		432.28		477.34	

As expected, the ΔE^{red} of 121.81 mV (0.4 V s⁻¹) and 91.24 mV (1.0 V s⁻¹) obtained in the presence of CO₂ are smaller than the value obtained from the slower scan rate of 0.1 V s⁻¹. The increase in scan rates outruns the reaction between reduced NQ and CO₂, hence less product is generated which results in a smaller difference of ΔE^{red} at the start and the end of the experiment.

Figure 22 shows the changes in the voltammetric behaviour of NQ in CO₂ saturated CH₃CN conditions over prolonged cycling with Ar blowing on the top of the solution. It is predicted that the one two-electron behaviour observed initially in the presence of CO₂ would revert to the two one-electron process over the course of the experiment after all the CO₂ had been consumed, as observed. While the quinone undergoes a reaction with CO₂, it is also possible that CO₂ would have been displaced by the Ar over time, resulting in the two one-electron CV observed at the 100th scan. Nevertheless, the quinone is still able to undergo a reaction while the solution was saturated with CO₂. The slow scan rate of 0.1 V s⁻¹ was used in conjunction with a higher quinone concentration (5 mM) and a larger WE surface (3 mm diameter) to facilitate the reaction and attempt to generate a significant amount of product for analysis using ¹H nuclear magnetic resonance spectroscopy. The NMR spectrum obtained is shown in Figure 23.

Figure 22. CVs of 5 mM NQ/50 mM Et₄NPF₆ in CO₂-saturated CH₃CN recorded at 0.1 V s⁻¹ scan rate with a 3 mm diameter planar GC WE at 25±2 °

Figure 23. ¹H NMR spectra of 5 mM NQ with 50 mM Et₄NPF₆ after 100 cycles in CO₂-saturated CH₃CN solution.

Solvent suppression ^1H NMR was utilised to obtain the ^1H spectrum shown in Figure 23. Et_4NPF_6 was used as the electrolyte as it exhibits only two signals and can facilitate the characterizations of products compared to $n\text{Bu}_4\text{NPF}_6$ which has four signals. Two additional signals at 6.68 and 7.44 ppm were observed after the experiment in CO_2 and not present in the control. This region is magnified and shown in Figure 24. The signals at 6.68 and 7.44 ppm display an integration ratio of 2:1. Attempts are currently ongoing in the assignment of the peaks and elucidation of the product formed. It is clear through the NMR data and CV experiments that a product is generated during the reduction of NQ in the presence of CO_2 .

Figure 24. Magnified ^1H NMR spectra of 5 mM NQ with 50 mM Et_4NPF_6 after 100 cycles in CO_2 -saturated CH_3CN solution.

4.7 Summary

In this study, we were able to determine that different intermediates are formed when NQ is reduced in the presence of CO_2 compared to in the presence of Ar. In-situ UV-Vis studies performed on the reduction of NQ under Ar conditions and under CO_2 conditions showed significant differences, which indicated that there is an interaction occurring between the reduced quinone and CO_2 . Initial CV studies had also shown that apart from the nucleophilicity of the quinone, the methyl groups present on the aromatic ring with the carbonyl groups causes a

significate steric hinderance that affects the ability of the quinone to attack CO₂. Substituents could be added onto the adjacent ring instead to provide an electron-donating inductive effect without blocking the oxygen atoms on the quinone. It is also noted that the reduced quinones could be either reacting directly with CO₂ (to form other products) or interacting through weaker non-covalent interactions. Although the products could not be determined from this study, the continuous CV cycling data as well as NMR spectrum showed that there is a compound generated during the reaction and this information could help with understanding the reaction mechanism quinones undergo in the presence of CO₂.

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Chapter 5

Anthraquinones as CO₂ Electrocatalysts

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5.1 Introduction

Anthraquinones are an abundant class of compounds in the group of natural substances, and 9,10-anthraquinone (AQ) is the most common sub-group present. The structure of AQ is derived from anthracene, with the addition of two carbonyl oxygen atoms in the 9- and 10-positions. Anthraquinone derivatives are widely used as dyes, both natural and synthetic, in areas such as textile dyeing and food.¹ They are also found in bacteria² and insects³ as biologically active compounds. In addition, they function as catalysts in many chemical processes, such as the manufacturing of hydrogen peroxide, based on their low redox potential.⁴

In this chapter, studies were done to further explore the use of anthraquinones, specifically 9,10-anthraquinone (AQ), and its ability to capture and convert CO₂. In comparison to the naphthoquinones, AQ has one more additional aromatic ring, which could perhaps bring about better stability for trapping CO₂ or alter the nucleophilic properties of the quinone. These would be furthered explored by examining the electrochemical behaviour of AQ in the absence and presence of CO₂.

5.2 Electrochemical Behaviour of Anthraquinones

CV experiments were performed on AQ in the absence and presence of CO₂, with the CV profiled shown in Figure 1.

Figure 1. CVs of 1 mM AQ/0.1 M $n\text{Bu}_4\text{NPF}_6$ in CH_3CN under Ar (black trace) and CO_2 (red trace) recorded at 0.1 V s^{-1} scan rate with a 1 mm diameter planar GC WE at $25 \pm 2^\circ \text{C}$.

Similar to the other quinones that have been investigated, under Ar conditions, AQ undergoes two one-electron reduction reactions to form the semiquinone first, followed by the dianion species. The $E_{\text{Q}/\text{Q}^{\cdot-}}^{\text{red}}$ occurs at $-1.30 \text{ V vs. Fc/Fc}^+$ while the $E_{\text{Q}^{\cdot-}/\text{Q}^{2-}}^{\text{red}}$ occurs at $-1.75 \text{ V vs. Fc/Fc}^+$, which is at a more negative potential than the naphthoquinones. Under CO_2 conditions, a single reduction peak at $-1.27 \text{ V vs. Fc/Fc}^+$ is observed and the second reduction peak is absent, as seen with the naphthoquinones as well. Having a more negative reduction potential would indicate that a greater amount of energy is required for reduction to occur. However, initial studies on AQ could serve as a precursor for future works, where substituents could be added onto the additional ‘vacant sites’ on its aromatic rings in order to modify the compound to make it more energy efficient for the reduction of CO_2 .

5.3 Reduction of Anthraquinone via CPE Experiments

Stepwise CPE experiments were also conducted to reduce AQ to its semiquinone and dianion states under Ar and CO_2 in CH_3CN in order to observe the stability of the reduced species within the timescale of the experiments.

Figure 2. CVs of 1 mM AQ/0.1 M $n\text{Bu}_4\text{NPF}_6$ in CH_3CN under Ar conditions recorded at 0.1 V s^{-1} scan rate with a 1 mm diameter planar GC WE at $25 \pm 2^\circ \text{C}$ before and after electrolysis.

Under Ar conditions, AQ undergoes two one-electron reduction reactions to form first the semiquinone, followed by the dianion at more negative potentials. AQ and its reduced species also display the typical quinone behaviour as reduction occurs. Similar to NQ, the CV profile shifts in the positive current direction after the first and second electron reduction, and the reason for its occurrence is as explained in chapter 4. For AQ, it appears that after the second electron reduction when the scan is then reversed and applied in the positive potential direction, a small oxidation peak is formed at around 0.12 V vs. Ag , which could be due to the formation of the dihydroquinone of AQ. The first electron peak also appears to have a slight decrease in current, but it still maintains the two one-electron reduction behaviour. Nevertheless, AQ and its reduced species still appear to be rather stable within the timescale of the experiment ($t \sim \text{mins}$)

Figure 3. CVs of 1 mM AQ/0.1 M $n\text{Bu}_4\text{NPF}_6$ recorded at 0.1 V s^{-1} scan rate in CO_2 saturated CH_3CN with a 1 mm diameter planar GC WE at $25 \pm 2^\circ \text{C}$ before and after electrolysis.

Under CO_2 conditions, Figure 3 shows the CV profile of AQ before and after the second electron reduction and the reduced species were stable within the time scale of the experiment ($t \sim$ mins). The oxidation peak that forms at around 0.12 V vs. Ag after the second electron reduction in Ar conditions is not present, further indicating that CO_2 helps to provide a stabilization effect on the reduced quinone, preventing it from undergoing side reactions. After the two-electron reduction, the solution was purged with Ar and the electrochemical behaviour of AQ was recorded and shown in the CVs in Figure 4.

Figure 4. CVs of 1 mM AQ/0.1 M $n\text{Bu}_4\text{NPF}_6$ in CO_2 -saturated CH_3CN recorded at 0.1 V s^{-1} scan rate with a 1 mm diameter planar GC WE at $25 \pm 2 \text{ }^\circ\text{C}$. Solid trace : CV measured after two electron reduction electrolysis, dashed trace : CV measured after reduced solution was purged with Ar for 15 minutes.

After purging the solution with Ar, the electrochemical behaviour of AQ differs from the typical quinone behaviour. The second reduction has lost its chemical reversibility, indicating that the reduced form of AQ has interacted in some way with CO_2 . A change in the colour of the solution from yellow to orange throughout electrolysis also shows that a reaction has occurred between CO_2 and AQ.

5.4 Using Methanol for Mixed Solvent System

The use of mixed solvent systems have been present for various chemical studies such as the study of thermodynamic and kinetic ion interactions,⁵ as well as to improve the solubility of compounds in the solvent of choice.⁶ A mixed solvent system is also a common technique used in recrystallisation, where one solvent is used to dissolve the compound, and the second solvent is used to induce crystallisation.

As hydrogen bonding occurs in the presence of methanol (MeOH), we attempted to add MeOH into our solvent system in order to examine if the effect of hydrogen bonding would help to improve the stability of the quinone- CO_2 adduct. Stabilising the reduced species would allow it

to be less susceptible to side reactions with external parameters or impurities, enabling the quinone to undergo the proposed catalytic reaction mechanism with CO_2 . MeOH is also an organic solvent and miscible with CH_3CN , making it a suitable solvent to work with.

5.4.1 CV Experiments

Figure 5 shows the CV data which compares the voltammetry behaviour of AQ in the absence and presence of CO_2 , as well as in CH_3CN only and in 50% CH_3CN and 50% MeOH solvent.

Figure 5. CVs of 1 mM AQ/0.1 M $n\text{Bu}_4\text{NPF}_6$ in varying conditions recorded at 0.1 V s^{-1} scan rate with a 1 mm diameter planar GC WE at $25 \pm 2^\circ\text{C}$.

Comparing the CV profiles under Ar, in the absence (black trace) and presence (blue trace) of MeOH, both the first and second reduction process shifts towards more positive potentials in the presence of MeOH, but the second reduction process shifts by a greater amount. Studies have shown that this occurs due to hydrogen bonding, with the second reduction process shifting by a greater amount due to the dianion undergoing much stronger and more extensive hydrogen bonding interactions.⁷ Next, in the CV profiles in $\text{CH}_3\text{CN}/\text{MeOH}$ in the absence (blue trace) and presence of CO_2 (red trace), the reduction potential shifts slightly more towards the positive potential, which further suggests that the presence of CO_2 provides a stabilisation effect

and makes it easier for the quinone to be reduced. Having more positive potentials would be useful in that lesser energy would be consumed for quinone to undergo reduction. This has interesting potential consequences in the area of energy generation. For example, the quinone could first be reduced in the presence of “waste” CO_2 (from industrial processes) to form the complexed dianion $[\text{Q}(\text{CO}_2)_2^{2-}]$, the CO_2 could then be removed by purging with an inert gas to form the non-complexed dianion (Q^{2-}). This would mean that the non-complexed dianion is being formed by around 0.5 V less energy than in the absence of CO_2 , and this excess “free” voltage could be used for electricity generation. However, for this process to be economically viable, it would also require the inert purging gas to be energetically efficiently recycled.

5.4.2 UV-Visible Spectroscopy

In order to compare the stability of the products formed and determine if MeOH helps to stabilize the reduced species, ex-situ UV-visible spectroscopy was performed by doing CPE reduction of the quinone using the electrolysis cell, and transferring the solution into the OSTLE UV-vis cell before measurements were taken at 30 mins interval over a period of 24 hours.

Figure 6. UV-vis spectra obtained of 1 mM AQ/0.1 M $n\text{Bu}_4\text{NPF}_6$ in 50% CH_3CN / 50% MeOH under Ar conditions after two electron reduction. First UV-vis scan (red) was taken immediately.

Figure 6 shows the UV data obtained after two electron reduction of AQ under Ar conditions in 50% CH₃CN / 50% MeOH. Upon the first UV scan, it appears that the dianion has already reverted back to the neutral quinone. It is possible that during the transfer of the solution from the electrolysis cell to the UV-vis cell, the solution may have been exposed to oxygen, resulting in the oxidation of the dianion back to the neutral quinone. This however has been taken into account for this experiment, as one of the aims was to observe if hydrogen bonding from MeOH could improve the dianion's stability. The hypothesis was that the presence of hydrogen bonding from MeOH could help to provide better stability for the dianion species such that it would be less reactive when exposed to a small amount of air. From the data obtained, it can be concluded that the presence of hydrogen bonding only is not enough to allow stability for the dianion species against the exposure of air.

Next, an UV-vis experiment was performed under CO₂ conditions in CH₃CN solvent to observe if the presence of CO₂ only would provide a better stabilising effect as compared to MeOH.

Figure 7. UV-vis spectra of 1 mM AQ²⁻/0.1 M *n*Bu₄NPF₆ in CH₃CN under CO₂ conditions. First UV-vis scan (red) was taken immediately, followed by next two scans at 30 mins interval

The UV spectrum of neutral AQ (black) was collected in the presence of CO₂, which is similar to the UV spectrum of AQ under Ar conditions, thus AQ also has to be reduced to its semiquinone or dianion species before a reaction can occur between CO₂ and quinones. Upon taking the first scan of the UV spectrum (after transferring the sample from the electrolysis cell into the UV-vis cell), there appears to be a change in spectrum compared to neutral AQ (Figure 7, red line). A new peak is formed at 212 nm and the peak at 325 nm has decreased in absorbance. An absorption gain at 380 nm above a broader absorption at 400 nm was also observed. The change in the spectrum only occurs when there is a reduction of AQ, thus it is likely that the spectrum obtained under CO₂ would correspond to AQ(CO₂)₂²⁻. Following the second scan, the reduced quinone has reverted back to the neutral quinone state and the spectrum remains at the neutral state from the third scan onwards. While the reduced species of NQ in CO₂ was stable over the 24-hour period, the dianion of AQ in CO₂ was only stable within the timescale of minutes. It could be possible that the interaction between the reduced species of AQ and CO₂ is not as strong as NQ with CO₂, thus the oxidation of AQ²⁻ back to the neutral quinone occurs more readily.

The following UV experiment was then conducted under CO₂ conditions in 50% CH₃CN / 50% MeOH to observe if the presence of both CO₂ and MeOH would help to further stabilize the reduced species.

Figure 8. UV-vis spectra of 1 mM AQ²⁻/0.1 M *n*Bu₄NPF₆ in 50% CH₃CN / 50% MeOH under CO₂ conditions over a period of 24 hours at 25±2 °C. First UV-vis scan (red) was taken immediately, followed by spectrum plots at every 5-hour intervals.

A similar spectrum was observed as the spectrum for AQ²⁻ under CO₂ in CH₃CN, but the addition of MeOH in the solvent appears to stabilize the reduced species against the small exposure of air as well as being stable over a 24-hour period. There is a formation of a broad peak at around 260 nm, and a loss of absorbance at 325 nm. The absorption gain at 380 nm over the broad absorption at 400 nm is also more pronounced compared to the spectrum under CO₂ in CH₃CN. Following this, the concentration of MeOH in the solvent was varied to observe if an increase in MeOH would increase the stability of the reduced species.

Figure 9. UV-vis spectra of 1mM AQ²⁻/0.1 M *n*Bu₄NPF₆ in a) 75% CH₃CN / 25% MeOH and b) 25% CH₃CN / 75% MeOH under CO₂ conditions over a period of 24 hours at 25±2 °C. First UV-vis scan (red) was taken immediately, followed by spectrum plots at every 5-hour intervals.

Table 1. Percentage change in absorption value at 380 nm over a 24-hour period for UV-vis experiment conducted under CO₂ in CH₃CN / MeOH solvent system

Solvent System	Change in absorbance at $\lambda = 380$ nm / %
75% CH ₃ CN / 25% MeOH	54.6
50% CH ₃ CN / 50% MeOH	48.4
25% CH ₃ CN / 75% MeOH	97.2

The percentage change in absorbance of the peak at 380 nm was used as an indicator for the stability of the reduced species, and the value is calculated by taking the difference in absorbance between the first and the last scan, divided by the absorbance value of the first scan and multiplying by 100. The values that were obtained are shown in Table 1. In a solvent system of 75% CH₃CN / 25% MeOH, it is expected that the reduced species would be less stable than in 50% CH₃CN / MeOH due to a lower concentration of MeOH available for hydrogen bonding. From the values in the table, the change in absorbance in 75% CH₃CN / 25% MeOH is greater than in 50% CH₃CN / MeOH, indicating that the decay of the reduced species occurs faster in 75% CH₃CN / 25% MeOH and thus less stable. Thereafter, the same experiment was repeated in 25% CH₃CN / 75% MeOH. Interestingly, while the same spectrum was observed, the change in absorbance is greater at 97.2%, which is higher than the values obtained compared to 75% CH₃CN / 25% MeOH and 50% CH₃CN / MeOH. A greater increase in MeOH may not proportionately increase the stability effects on reduced AQ, and a balance has to be achieved on the solvent composition in order to optimise the stability effects.

5.4.3 CPE Experiments

CPE experiments were then performed in order to observe if the reduced AQ species would be stable on longer timescales ($t \sim$ mins) in the presence of MeOH. In 50% CH₃CN / 50% MeOH, the CV data obtained showed that the first and second reduction peaks shift to a more positive potential to give one two-electron reduction peak. In order to aid differentiating the CV peaks between that in Ar and in CO₂, MeOH was added in an amount that was significant, but not great enough to merge the two reduction processes so that the quinone behaviour would show its typical two one-electron reduction. Experimental data obtained by previous members of the group have shown that for 1mM of quinone, 25-50 mM of MeOH can be used without observing the merging of the second and first reduction processes. For this CPE experiment, 37.5 mM of MeOH was added to the solvent to observe if the presence of MeOH would help to stabilise the reduced species and facilitate the reaction between AQ and CO₂.

Figure 10. CVs of 1 mM AQ/0.1 M $n\text{Bu}_4\text{NPF}_6$ in CH_3CN with 37.5 mM MeOH recorded at 0.1 V s^{-1} scan rate with a 1 mm diameter planar GC WE at $25 \pm 2 \text{ }^\circ\text{C}$.

In this experiment, AQ first undergoes stepwise reduction in Ar and when it reaches the dianion state, CO_2 was then bubbled into the solution of AQ^{2-} . Figure 10 shows the CV data during the bulk electrolysis under Ar conditions. A shift in the current of the CVs were observed, and the oxidation peak that was previously noted at 0.12 V vs. Ag during the CPE reduction of AQ in CH_3CN , is also observed in this CPE data but at more positive potentials (0.4 V vs. Ag) and has a smaller peak current. This could indicate that the presence of MeOH helps to increase the stability of AQ^{2-} and reduces the formation of side products. After the two-electron reduction, electrolysis was halted, and CO_2 was bubbled into the solution for 7 minutes. The two-electron reduction process subsequently merged into one, and the background current decreased to the zero value, suggesting that no reduced forms were present. Ar was then re-bubbled into the solution to monitor the interactions between CO_2 and AQ.

Figure 11. CVs of 1 mM AQ/0.1 M $n\text{Bu}_4\text{NPF}_6$ in CH_3CN with 37.5 mM MeOH recorded at 0.1 V s^{-1} scan rate with a 1 mm diameter planar GC WE at $25 \pm 2 \text{ }^\circ\text{C}$.

As shown in Figure 11, upon re-bubbling the CO_2 saturated solution with Ar for 7 minutes, the typical quinone behaviour is regenerated. This suggests that while MeOH helps in the stabilisation of the reduced species, perhaps the presence of hydrogen bonding may have hindered the dianion species from reacting irreversibly with CO_2 . Studies have been performed on quinones to show that the reduced quinone species are able to undergo strong hydrogen bonding with water, even in trace amounts.⁸ Alcohols are also shown to be able to form hydrogen bonds with quinones as that seen with water.⁹ It is likely that during the formation of the dianion species, AQ^{2-} , it forms hydrogen bonds with MeOH. Thus when CO_2 is bubbled into solution after the dianion species are formed, the hydrogen bond interaction may hinder the quinone dianion species from reacting with CO_2 . Through the course of bubbling CO_2 , small amounts of air may have entered the solution and reacted with the reduced species, resulting in the drop of the background current to the zero value. Further bubbling of the solution with Ar regenerates the typical quinone behaviour since AQ^{2-} was unable to effectively react with CO_2 . Thus from this experiment, we can conclude that for quinones to effectively react with CO_2 , CO_2 has to be dissolved in solution before the formation of the dianionic species.

5.5 Summary

This study of AQ as an electrocatalyst focused more on its efficacy rather than the efficiency. One limitation that was encountered was that the solubility of AQ in CH₃CN was fairly low, experimentally determined to be 5 mM. This would hinder potential future studies on the compound since the quinone has to be soluble in order for it to interact with CO₂ in solution. Future works in this area could include functionalisation of the aromatic rings to increase solubility, and also to adjust the chemical properties to enhance the interactions between CO₂ and AQ.

Using MeOH as a co-solvent has potential in increasing the stability of the reduced AQ species, however as MeOH is one of the CO₂ reduction products, the presence of MeOH in the solvent system could affect the calculation of the faradaic efficiency if future work show that methanol is produced as a product. Thus what could be done is to find another solvent that provides a form of hydrogen bonding interaction for the quinone and yet is not a potential product of CO₂ reduction.

Through this study, it is shown that quinones in general could aid in the capture of CO₂. Further studies should focus on increasing the efficiency of AQ as an electrocatalyst, as well as to identify a suitable solvent system to drive the reduction of CO₂.

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Chapter 6

Conclusion

6.1 Conclusion

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6.1 Conclusion

In this thesis, a mechanism of CO₂ capture and conversion was proposed and investigated in a bid to mitigate the adverse effects of CO₂ emission on global climate patterns and possibly as a way of reversibly lowering reduction potentials of quinones as a way of generating electricity. In chapter 4, three naphthoquinones were studied on, but only the parent quinone NQ was found to be the most effective in capturing and converting CO₂. It appears that the quinone and CO₂ reaction can be distinguished into two pathways, the first is an interaction which generates the Q(CO₂)₂²⁻ intermediate and the second pathway allows CO₂ to further react and form the reduction products. Despite being the most nucleophilic, DMNQ seems to only be able to interact with CO₂ to form the intermediate compound and not react with CO₂, probably due to the steric hindrance caused by the methyl groups. It is suspected that a hydrogen donor had been produced during the electrochemical cycling of NQ in the presence of CO₂ due to the significant shift of E_{Q2} towards more positive potentials at the end of the experiment after removal of CO₂. ΔE^{red} was noted to decrease with faster applied scan rates, indicating that less products were generated. This occurs because the increase in scan rates partially outrun the kinetics of the reaction between reduced NQ and CO₂ as well as provide a shorter timeframe for conversion into the product.

In chapter 5, AQ was investigated for its electrocatalytic abilities, and how hydrogen bonding properties of the solvent could play a part in the reaction as well. AQ has shown some potential in being a catalyst for CO₂ capture and conversion from its electrochemical behaviour despite the limits on its solubility. The use of an additional solvent (methanol) was also shown to provide an extra stability effect for the reduced quinone species. This could be taken into consideration when developing a system involving quinones. From the results obtained in these two studies, it is promising to know that the reduction of CO₂ could be achieved at a lower applied potential compared to direct reduction of CO₂, and further exploration with this data could help with building an efficient system for converting CO₂ into more useful products.

The understanding of the effects of nucleophilicity is advantageous for the electrochemistry of quinones in the presence of CO₂, thus it is worthy to look at other more

nucleophilic derivatives of NQ such as those with substituents on the adjacent ring. Different substituent groups on the quinone such as ether, hydroxyl and amine groups, all of which are more electron donating, can also be explored. Increasing the solubility of the quinone can also be a factor to consider when adding these substituents.

The supporting electrolyte assists in the stabilisation by balancing the charge in the reaction system. However, the alkylammonium electrolytes used in this study are NMR active which poses some challenges in the accurate characterization of the reduction products. The high amount of electrolyte used (100 times more in excess of the quinone) means that dilution is necessary prior to injection into the liquid chromatography-mass spectrometry (LC-MS). Thus other electrolytes could be identified that would allow for more appropriate and easier detection of the products.

Apart from hydrogen donors, gaseous products can also be formed during the reduction of CO₂. CO is a possible product that can be formed from a two-electron reduction of CO₂, and CO can be used in the Fischer-Tropsch process where it is converted into useful hydrocarbons. Due to difficulties in performing electrolysis under a gas-tight environment, we were unable to determine if there were any gaseous products formed from our catalytic mechanism. However it is an area that is worth exploring in future in order to do a comprehensive study on the products that could be formed from our system.

While much work still remains to be done, the results presented led us to believe that quinones have the potential to act as electrocatalysts for the reduction of CO₂. With further investigation and product determination, the reaction mechanism could be deduced and perhaps aid in the development of a system that can efficiently convert CO₂ into more useful materials.