

CATALYSIS OF ELECTROCHEMICAL BIOMASS VALORISATION

Thesis submitted for the degree of Doctor of Philosophy

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To my Uncle for first introducing me to the magic of science at a young age.

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Declaration

The material described in this thesis is a result of my own work unless stated otherwise. Experiments were completed at Imperial College London between October 2019 and January 2023 under the supervision of Dr Ifan E. L. Stephens, Professor Maria Magdalena Titirici, Dr Soren B. Scott, and Dr Stefano Mezzavilla (between October 2019 and May 2021).

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Abstract

Catalysis of Electrochemical Biomass Valorisation

Zamaan Mukadam

The climate crisis has come to the attention of many scientists, lawmakers, and global companies in recent years. Replacing petrochemicals with refined waste biomass as a sustainable chemicals source has become an attractive option to lower global carbon emissions. Popular methods of refining lignocellulosic waste biomass use thermochemical means which have significant environmental downsides, that can be overcome by using electrochemistry instead. This can revolutionise the way many chemicals are produced today.

Guided by theoretical calculations, this work begins by demonstrating the electrochemical production of the biofuels 2-methylfuran and hydrofuroin via the electroreduction of furfural, using synthesised single-atom electrocatalysts, and Cu foil electrodes. This study revealed that a proton-coupled electron transfer (PCET) mechanism is the favoured method of electrochemical reduction under acidic (pH 1) conditions.

New electrochemical processes to produce amines from 5-hydroxymethylfurfural (HMF) are explored using hydroxylamine as a nitrogen source, in an electrochemical reductive amination reaction. A range of metal surfaces were tested with Ag electrodes exhibiting the best reductive amination activity in mild, aqueous conditions. A new electrochemical synthesis process is demonstrated whereby an amino acid 5-(aminomethyl)furan-2-carboxylic acid (AFCA), is produced by combining Ag cathodes with MnO_x anodes to independently convert the functional groups of HMF without the need to separate intermediates between reactions.

Lastly, the development of a new metal-free electrocatalyst is detailed by immobilising (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) onto an electrode surface, aiming to oxidise HMF into the monomer 2,5-furandicarboxylic acid (FDCA). For the first time in literature, selective electrochemical production of 5-formyl-2-furoic acid (FFCA) is successfully reported. Methods are discussed to try and steer the selectivity from FFCA to FDCA, which can be used as a replacement monomer for terephthalic acid in PET polymers.

Due to the significance of the work presented here, the commercialisation of electrochemical biomass valorisation is brought a step closer.

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Abbreviations

δ	NMR chemical shift
μ	micro
$\Delta_f G^0$	Standard Gibbs energy of formation
j	Current density
N_a	Avogadro's constant
A_r	Relative atomic mass
$^\circ$	degrees
2-MF	2-methylfuran
2-MeTHF	2-methyltetrahydrofuran
5-MF	5-methylfurfural
ACT	4-acetyl-TEMPO
AFCA	5-(aminomethyl)furan-2-carboxylic acid
BDD	Boron doped diamond
BHH	5,5'-bis(hydroxymethyl)hydrofuroin
BHMF	2,5-Bis(hydroxymethyl)furan
CoPc	Cobalt phthalocyanine
CO ₂ RR	Carbon dioxide reduction reaction
CuPc	Copper phthalocyanine
CV	Cyclic voltammetry
DAMF	2,5-bis(aminomethyl)furan
DFF	2,5-diformylfuran
DMeF	Dimethylfuran
DMF	Dimethylformamide
DFT	Density functional theory
DMSO	Dimethylsulfoxide
U^0	Standard equilibrium potential
EG	Ethylene glycol
ECH	Electrochemical hydrogenation
EC-MS	Electrochemistry mass spectrometry

ECO	Electrochemical oxygenation
EDC	<i>N</i> -(3-dimethylaminopropyl)- <i>N</i> '-ethylcarbodiimide hydrochloride
EDX	Energy dispersive X-ray
EPR	Electron paramagnetic spectroscopy
eV	Electron volt
<i>F</i>	Faraday constant
FA	2-furfurylamine
FAL	Furfuryl alcohol
FDCA	2,5-furandicarboxylic acid
FE	Faradaic efficiency
FF	Furfural
FFCA	5-formyl-2-furoic acid
HAC	2-hydroxyacetaldehyde
HAADF-STEM	High-angle annular dark-field imaging-scanning transmission electron microscopy
HDO	Electrochemical hydrodeoxygenation
HER	Hydrogen evolution reaction
HFO	5-hydroxy-2(5H)-furanone
HMFA	5-(aminomethyl)furan-2-yl)methanol
HMF	5-hydroxymethylfurfural
HMFA	5-hydroxymethyl-2-furancarboxylic acid
HPLC	High performance liquid chromatography
KB	KetjenBlack EC600D carbon black
LA	Levulinic acid
LC-MS	Liquid chromatography-mass spectrometry
LPEI	Linear poly(ethylenimine) films
LSV	Linear sweep voltammetry
MA	Maleic acid
MEA	Membrane electrode assembly
MOF	Metal-organic framework
MWCNT	Multiwalled carbon nanotubes

m/z	mass to charge ratio
n	Moles
NIST	National institute for standards and technology
NDI	Napthalene diimide
NMR	Nuclear magnetic spectroscopy
NOESY	Nuclear Overhauser effect spectroscopy
OCP	Open circuit potential
OER	Oxygen evolution reaction
ORR	Oxygen reduction reaction
PCET	Proton-coupled electron transfer
PE	Polyethylene
PEF	Polyethylene furanoate
PEEK	Polyether ether ketone
PET	Polyethylene terephthalate
PMI	Process mass intensity
PP	Polypropylene
PS	Polystyrene
PU	Polyurethane
PVC	Polyvinylchloride
Q	Total charge passed
qNMR	Quantitative nuclear magnetic spectroscopy
R	Molar gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)
RDE	Rotating disc electrode
RDS	Rate determining step
RHE	Reversible hydrogen electrode
SAM	Self-assembled monolayer
SDS	Selectivity determining step
SEM	Scanning electron microscopy
Sulfo-NHS	<i>N</i> -hydroxysulfosuccinimide sodium salt
T	Temperature (K)
TAP	2,4,6-triaminopyrimidine

TEM	Transmission electron microscopy
TEMPO	2,2,6,6-tetramethylpiperidin-1-yl)oxyl
TOF	Turnover frequency
ToF-SIMS	Time of flight secondary ion mass spectroscopy
TPA	Terephthalic acid
UV-Vis	Ultraviolet-visible
VCX-72	Vulcan carbon black
wt%	Percentage by weight
XPS	X-ray photoelectron spectroscopy
z	Electrons transferred per mole

List of Publications

The results presented in this thesis have either been published in peer-reviewed articles, or the relevant manuscripts are in preparation, and are listed below:

1. **Z. Mukadam**‡, S. Liu‡, A. Pedersen, J. Barrio, S. Fearn, S. Ch. Sarma, M. Titirici, S. B. Scott, I. E. L. Stephens, K. Chan, S. Mezzavilla. Furfural Electrovalorisation Using Single-atom Molecular Catalysts. *Energy Environmental Science*, 2023, **16**, 2934–2944.
2. S. Liu‡, **Z. Mukadam**‡, S. B. Scott, S. Ch. Sarma, M. Titirici, K. Chan, N. Govindarajan, I. E. L. Stephens, G. Kastlunger. Unravelling the reaction mechanisms for furfural electroreduction on copper. *Energy Environmental Science Catalysis*. 2023, **1**, 539–551.
3. **Z. Mukadam**, S. Liu, S. B. Scott, Y. Zhou, M. Bidwell, G. Kastlunger, M. Ryan, M. Titirici, I. E. L. Stephens. Direct Electrosynthesis of Amino Acid from a Biomass Derivative. (in preparation).
4. S. Liu‡, **Z. Mukadam**‡, A. Pedersen, J. Barrio, M. Titirici, G. Kastlunger, I. E. L. Stephens. Bridging outer- and inner-sphere electrosynthesis via single atom catalysts for furfural reduction. 2023, (in preparation).
5. **Z. Mukadam**‡, M. Bidwell‡, S. B. Scott, Y. Zhou, C. Liang, Y. Dang, M. Roessler, M. Ryan, M. Titirici, S. Mezzavilla, I. E. L. Stephens. Electrochemical production of FDCA using a novel metal-free electrocatalyst. 2023, (in preparation).
6. **Z. Mukadam**, M. Bidwell, T. Bennet, M. Titirici, I. E. L. Stephens. TEMPO immobilisation onto a macrocycle for heterogenous electrochemical FDCA production, 2023 (in preparation).

‡ These authors contributed equally.

1 | The Petrochemical Industry Needs Replacing

At present, many useful chemicals that are used in everyday life are sourced from petrochemicals, ranging from fuels, pharmaceuticals, adhesives, and polymers.¹ The refinement of crude oil and the subsequent use of petrochemical products are associated with greenhouse gas emissions which result in well-publicised detrimental impacts on the Earth's climate.² The climate crisis has highlighted the urgent need to phase out the use of fossil fuels if humanity is to avoid a climate catastrophe, by keeping global temperature rises below 1.5 °C to prevent non-reversible negative effects to the environment. As a measure to prevent this, the countries that attended the recent COP26 conference agreed to phase out the use of coal as an electricity source by 2030,³ as well as reach a net-zero emissions target as soon as possible. Whilst global warming will not be the focus of this thesis, it is still important to highlight the urgent need to lower our dependence on petrochemicals. An ideal scenario would be to stop extracting fossil fuels completely, however, this would require us to find an alternative source of chemicals which will form the focus of this thesis.

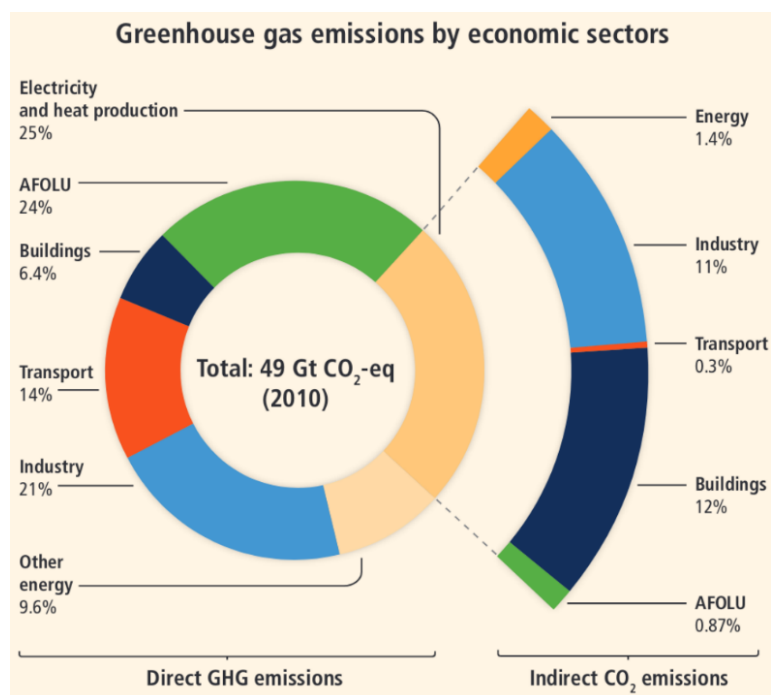


Figure 1.1. Greenhouse gas emissions by percentage, from economic sectors.⁴ AFOLU - Agriculture, Forestry and Other Land Use

Whilst the chemicals that are obtained from crude oil are useful for societal needs (**Figure 1.1**),⁴ their extraction, refinement, and the eventual disposal of petrochemical waste pose significant environmentally damaging problems. These problems must be faced head-on as the potential

consequences can be detrimental to future generations. Global crude oil production has been in the range of about 80-90 million barrels a day for the last few decades⁵ and is used to maintain a growing industrial sector and population. For this thesis, the focus will be centred on the issues of fuels and polymers, which are two of the most important and problematic products obtained from crude oil.

1.1 The Issues with Fuels

About 55% of a 45-gallon (204.5 L) barrel of crude oil is used for fuels (**Figure 1.1.1**)⁶ making them one of the most popular petrochemical products. In 2010, the U.S. Energy Information Administration reported that it required 553×10^{18} J of energy per year to power the world's industry, and predicted the demand to increase to 865×10^{18} J in 2040.⁷ The majority of this energy (>68% in 2014) comes from crude oil products due to them being one of the cheapest sources of electricity.⁸ Popular fuels like jet-fuel (kerosene) and diesel, which are mixtures of straight-chain hydrocarbons, are burnt in combustion engines to power vehicles used for transport and industry. However, the combustion of these fuels is associated with the well-publicised increase in carbon dioxide (CO_2) – a greenhouse gas which contributes towards the global climate crisis.⁹ As worldwide economic growth and demand for energy increases, more fuels are needed to sustain the demands of global economies which subsequently leads to the ever-increasing amounts of fuel consumption.

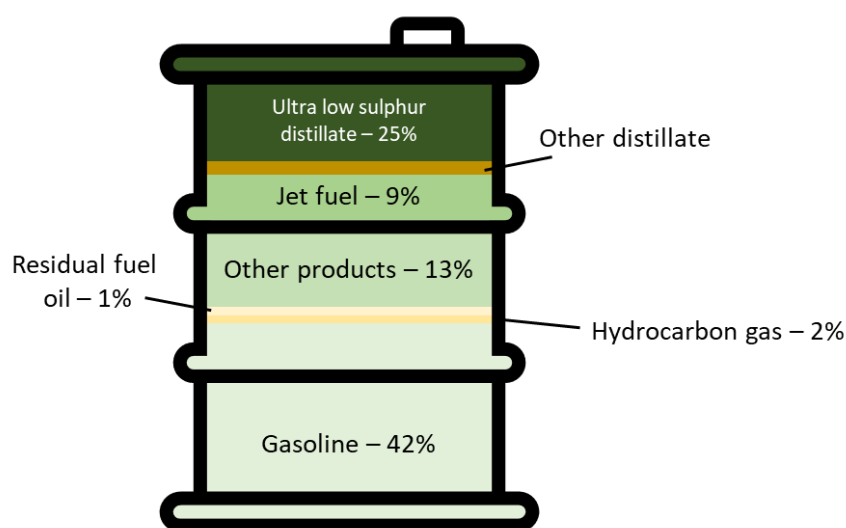


Figure 1.1.1. Distribution of petroleum products obtained from a 45-gallon barrel of crude oil. Numbers obtained from reference.⁶

For the aviation industry, the International Air Transport Association (IATA) reported that 95 billion gallons of jet fuel (4.3×10^{11} L) was used in 2019 alone.¹⁰ Measures to decrease carbon emissions from

the aviation industry have been proposed such as more efficient aircraft, the use of biofuels, and improving air traffic management.¹¹ To decrease global carbon emissions from vehicular transport, the use of alternative cleaner fuel sources can solve this problem which is more appealing than an unlikely scenario whereby vehicular transport is vastly limited instead. In this respect, biodiesel has attracted interest as an alternative fuel source, so much so that in France, bioethanol constitutes up to 20% of fuels in vehicles.¹² While this may sound promising, the amount of land needed to produce the necessary amounts of biofuel for global transportation needs to be considered. In this regard, completely replacing fossil fuels with biofuels may not be too feasible, as limitations are set on the amount of land needed for eventual reforestation, as well as growing food for the population.

The complete elimination for requiring fossil fuels may be possible by switching to electric vehicles powered by batteries instead. Electric vehicles are becoming more popular and avoid the need to directly burn fossil fuels to power them; however, they have their own drawbacks, as the popular Lithium-ion batteries required to power them are expensive and have problems with scalability.¹³ In addition, whilst green energy is in its relative infancy, the power needed to charge these vehicles is likely to come from fossil fuels themselves, although it should eventually be possible to power these vehicles using solar energy and other green sources.¹⁴

Unfortunately, the aviation industry cannot realistically be electrified. For example, a transatlantic flight would require so many batteries that the aircraft would weigh too much for this to be feasible.¹⁵ Hence a new alternative for cleaner aviation fuels is required. Recently, some planes have completed flights using 100% waste fuels from cooking oil,¹⁶ but this is not feasible on the large-scale due to the sheer number of aviation fuels used on an annual basis. Therefore, an opportunity arises as a market opens for jet-fuels from alternative sustainable sources.

1.2 The Issues with Polymers

Polymers are some of the most important materials that are used in everyday life for packaging, adhesives, and clothing.^{17,18} Polymer production has increased exponentially over the last few decades (**Figure 1.2.1a**)¹⁹ and is only predicted to rise further. Associated problems with increased polymer production appear when discussing how best to get rid of polymer waste. A total of 275 million metric tonnes of polymers were produced in 2010, with up to 12.7 million metric tonnes ending up in oceans, negatively affecting ecosystems.²⁰ Waste polymer incineration for electricity and heat generation is used in the European Union once reusability and recyclability are no longer an option, which can introduce CO₂ into the atmosphere.²¹ The incineration of halogen-containing polymers such as polyvinylchloride (PVC) is especially problematic as they can introduce chlorine radicals into the atmosphere which catalyse the destruction of the ozone layer.²² A popular method of dealing with

polymer waste is by burying in landfill sites; however, this method is not as effective as recycling and can be more environmentally damaging than incineration, due to the methane emissions from landfills being a worse greenhouse gas than CO_2 .²³ The main culprits of polymer waste include non-biodegradable addition polymers such as polyethylene (PE), polypropylene (PP), and polystyrene (PS), which take hundreds of years to biodegrade due to the sp^3 hybridised C-C backbone making natural degradation challenging. Still, in its relative infancy, methods studying the degradation of C-C backbone polymers are currently a hot area of research with different microorganisms being explored to tackle this.²⁴

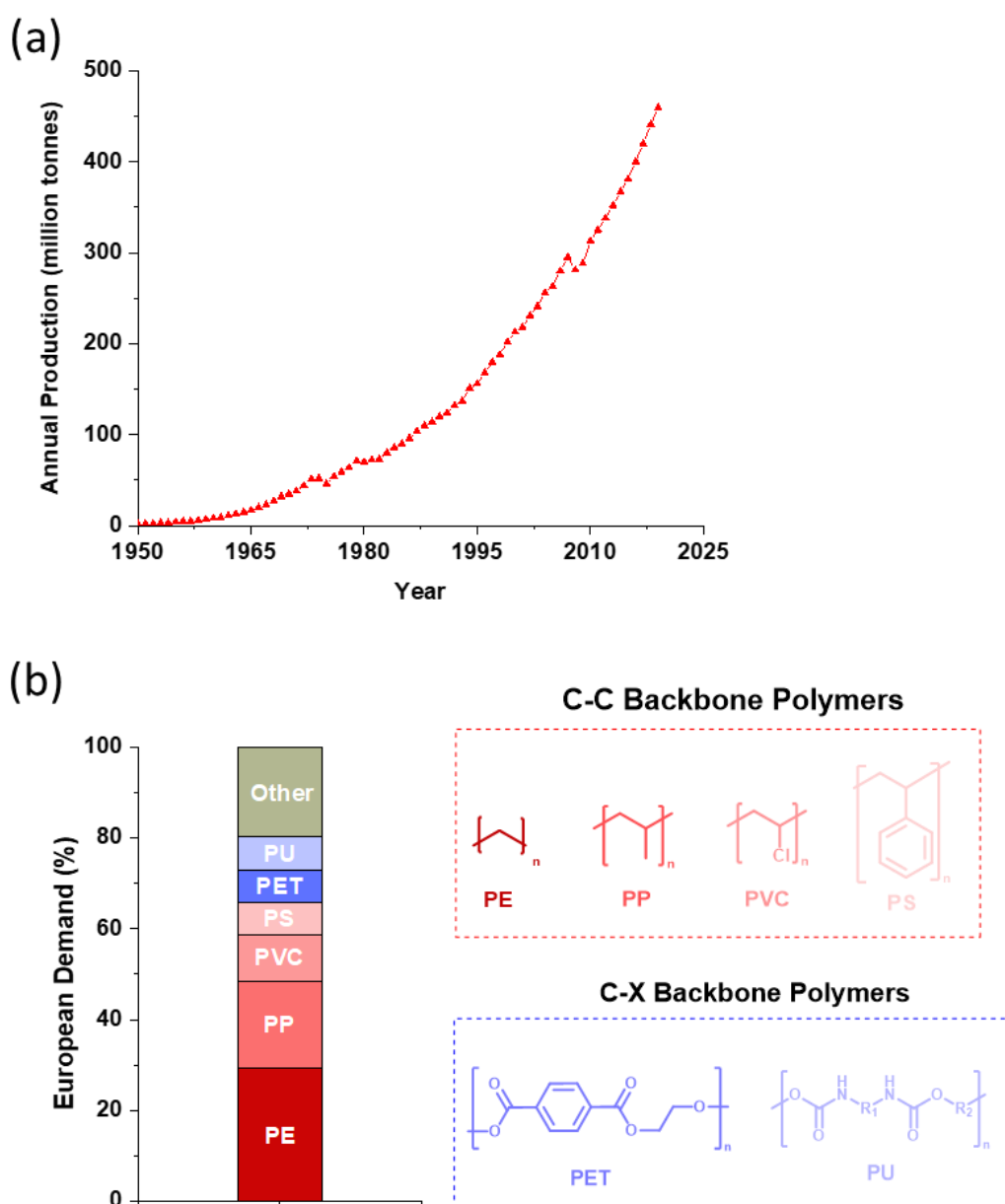


Figure 1.2.1. (a) Global primary plastics production from 1950 – 2015. Production has increased exponentially and is predicted to rise further. Graph produced from data points from reference.¹⁹ (b) Most popular C-C and C-X backbone polymers (where X is a heteroatom) produced as a percentage of European demand. Figure data points are taken from reference.²⁵

Condensation polymers containing C-X backbones (where X represents a heteroatom) can be converted back into their monomers after an acid/alkali catalysed depolymerisation.^{26,27} Condensation polymers have gained popularity with polyethylene terephthalate (PET) being the most popular polyester produced today with 30.47 million metric tonnes produced in 2019,²⁸ and is mostly used in the beverage packing industry. After use, the ester bond linkages in PET can be hydrolysed to recover the monomers which can be used to make new products. However, one of the monomers of PET, terephthalic acid (TPA), is obtained from the oxidation of *p*-xylene which itself is sourced from non-renewable petrochemical feedstock. The other monomer, ethylene glycol, has the potential to be obtained from sustainable sources such as during bioethanol production.²⁹ It is currently not possible to obtain TPA using similar methods due to the difficulty in synthesising the benzene ring, however, some Diels-Alder reactions starting from furan-based carbohydrates have been published, which show some promise in synthesising this monomer.³⁰ It would be beneficial to avoid these complex syntheses and hence preferable to phase out the use of PET into alternative polymers with similar thermochemical properties such as polyethylene furanoate (PEF). In PEF, the benzene ring is replaced by a furan ring by using 2,5-furandicarboxylic acid (FDCA) as a replacement monomer (**Figure 1.2.2**), which can be sustainably sourced from biomass,^{31,32} lowering the demand for *p*-xylene from petrochemicals. Replacing the benzene ring in PET with a furan ring has been shown to improve thermal stability because of the permanent dipole and non-linear structure of FDCA.³³ PEF exhibits a lower melting point compared to PET meaning less energy is required to melt down waste PEF for recycling.³⁴ In addition, PEF has a greater tensile strength, which means less material would be required to produce plastic bottles by saving materials using thinner-walled bottles.

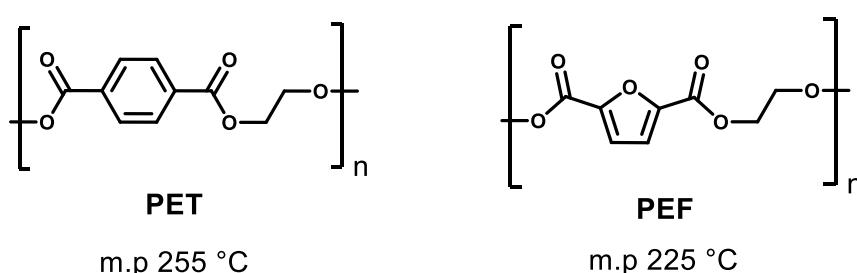


Figure 1.2.2. Structure of commercial PET polyester and its furanic counterpart PEF, with melting points of each polyester. Melting points obtained from reference.³⁴

It is without dispute the present methods of producing fuels and polymers are currently unsustainable, hence another source for these chemicals must be found. The ideal sources of new chemicals require them to be abundant, a waste product, and inedible. One potential source of chemicals which has garnered a lot of attention is lignocellulosic biomass which fills these criteria.

1.3 Biomass and Platform Chemicals

Biomass can provide us with chemicals that can replace the ones we obtain from crude oil.³⁵ About 170 billion metric tonnes of biomass is produced every year by photosynthesis, with about 75% of this consisting of carbohydrates, yet only 3-4% of this is used by humans for food and other uses.³⁶ This is a vastly greater amount of carbon in comparison to the ~5.25 billion metric tonnes of crude oil extracted annually. In addition, municipal biomass waste constitutes over 60% of global waste production including paper, food, and plant waste.³⁷ Lignocellulosic biomass can be extracted from municipal biomass waste and is made up of a combination of hemicellulose (15-30%), cellulose (40-50%), and lignin (15-30%) (**Figure 1.3.1**).³⁸ Hemicellulose is a biopolymer consisting of five and six membered carbohydrate monomers which can be hydrolysed into monosaccharides including glucose, xylose, and mannose.³⁹ Further hydrolysis produces useful furanic and straight chain 'platform chemicals' which can be defined as chemicals that can undergo a variety of chemical reactions to produce even higher valued chemicals.

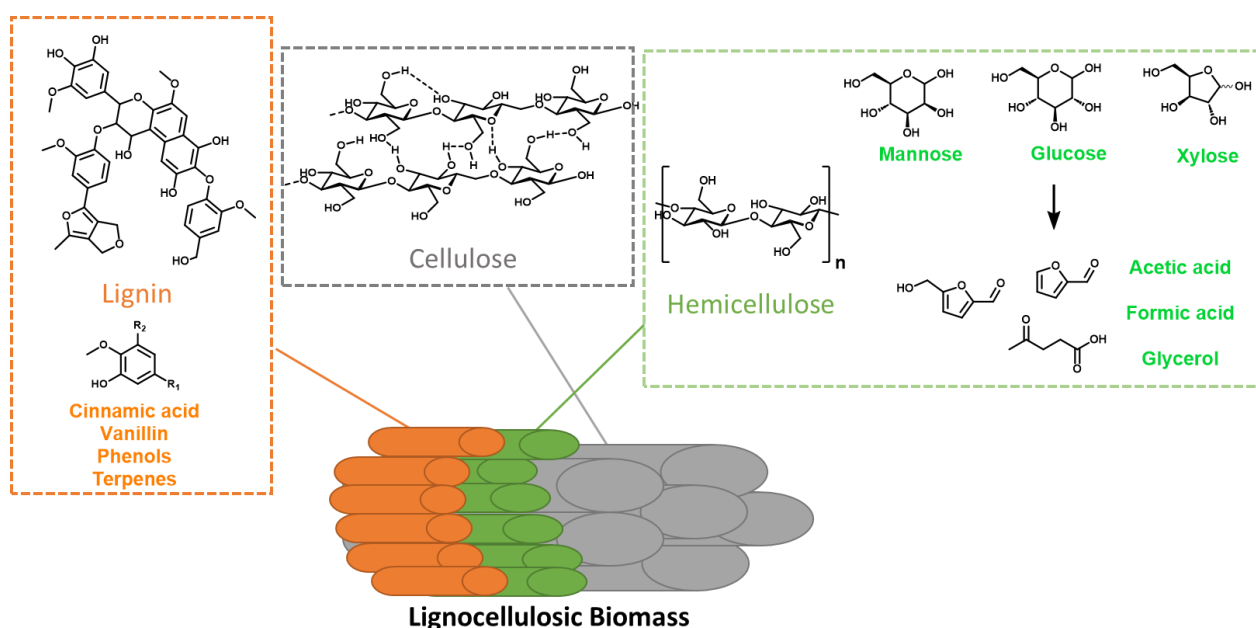


Figure 1.3.1. Possible useful chemicals that are available from lignocellulosic biomass.

In an ideal future scenario for a greener world, the plethora of chemicals which are currently sourced from crude oil refineries are instead derived from biomass, creating a 'biorefinery'. This concept was developed during the late 1990s and is currently defined by the U.S Department of Energy as a processing plant where biomass feedstock is upgraded into a spectrum of valuable products.⁴⁰ The biorefinery encompasses many novel organic chemical reactions, processes, technologies, and

catalysts needed to synthesise chemicals which can replace petrochemicals. The work in this PhD project will focus on novel reactions in the biorefinery utilising electrochemistry to replace the thermochemical synthesis for biomass-derived platform chemicals, to lower the overall carbon footprint of chemical synthesis. Consequently, this can be called the 'electrochemical biorefinery'. The resulting products of the reactions from the electrochemical biorefinery can be used to serve different purposes including as fuels, solvents, polymers, and others.⁴¹ Platform chemicals that can be upgraded include furanic compounds (C_{5-6} chemicals containing a furan ring) such as 5-hydroxymethylfurfural (HMF), furfural, as well as straight-chain C_5 platform chemicals such as levulinic acid (LA), and C_2 chemicals including ethylene glycol (EG).

HMF – HMF is a C_6 furanic compound (**Figure 1.3.2**) produced from the dehydration of hexose sugars and can be oxidised to produce FDCA.⁴² As briefly mentioned before, this resultant dicarboxylic acid has attracted attention as it can be used as a replacement monomer for terephthalic acid in PET polymers, and was even identified by the U.S. Department of Energy as one of the most important chemicals for a sustainable future.⁴³ Aside from uses in polymers, the reduction of HMF can yield dimethylfuran (DMeF), which has a high energy density and can be used as a biofuel.⁴⁴ Ring opening reactions are also possible with HMF which result in aliphatic monomers including 1,6-hexanediol, and straight chain hydrocarbons such as hexane which can be used as a solvent or fuel.⁴⁵ The library of potential compounds available from HMF and its decarboxylated C_5 relative, furfural, makes this platform chemical a sleeping giant with regards to one day replacing petrochemicals as our main chemicals source. The upgrading of HMF is not just limited to molecular redox reactions. A larger library of compounds can also be formed by coupling HMF to other small molecules to make larger C_{6+} compounds with diverse uses.⁴⁶

Whilst furfural is produced in quantities of about 0.25 million metric tonnes per year through polysaccharide hydrolysis,³⁵ the industrial scale-up of HMF production has not been yet established and so is not produced in the large quantities needed to completely replace petrochemicals as our main chemicals source. In addition, HMF is unstable and even the smallest impurities can result in the degradation of HMF into humin oligomer products,⁴⁷ making long-term storage an issue. The work being done to produce industrial amounts of HMF is still in its relative infancy, although there have been ventures by the companies Avantium⁴⁸ and Voltachem⁴⁹ to produce large amounts of HMF and FDCA. However, undisclosed reasons have seen them be either stopped or are not at the required quantities yet for meaningful change.

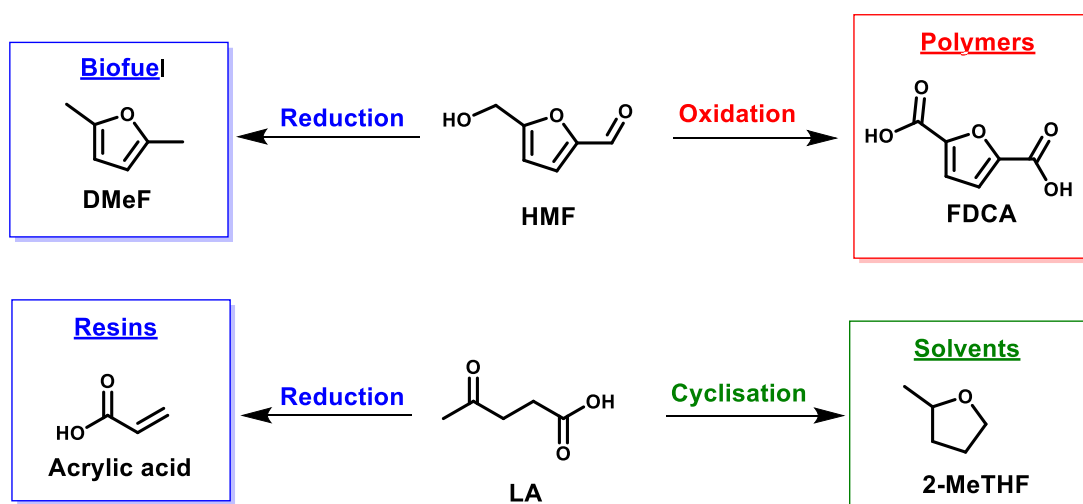


Figure 1.3.2. Examples of possible families of products available from the platform chemicals HMF and levulinic acid (LA) into useful families of chemicals.

Levulinic acid (LA) and ethylene glycol (EG) – LA is a C₅ aliphatic ketoacid with an annual production of 3820 metric tonnes (2020).⁵⁰ LA can be used as a liquid fuel itself or can be upgraded into valerate esters for fuel additives.⁵¹ LA can also be converted into 2-methyltetrahydrofuran (2-MeTHF) after cyclisation which can be used as a solvent (**Figure 1.3.2**).⁵² Smaller polyols such as EG can be used as a monomer in polyesters but can also be oxidised to produce oxalic acid and glycolic acid which have uses in polymers, pesticides, and skincare products.⁵³ The global demand for EG reached 25 million metric tonnes in 2014 with about 58% of this being used in PET.⁵⁴ The production of oxalic acid⁵⁵ and glycolic acid have increased over the last few decades, with the market size of glycolic acid reaching USD\$ 159.6m in 2015,⁵⁶ and projections expecting this to increase over the coming years.

EG can be produced via steam cracking of ethane,⁵⁷ as well as by reacting ethylene oxide with water.⁵⁸ EG can also be sourced from biomass through the hydrogenolysis of sorbitol and other sugars.⁵⁴ Obtaining EG from the hydrolysis of waste PET is also attractive and can lead to a circular economy whereby waste PET or PEF can be used to serve other purposes aside from recycling into new plastics. The total production of crude oil and biomass is depicted in **Figure 1.3.3** alongside the annual production of EG, furfural, and LA. From this, we see that there is a realistic opportunity to decrease crude oil production and replace some of the products from biomass instead.

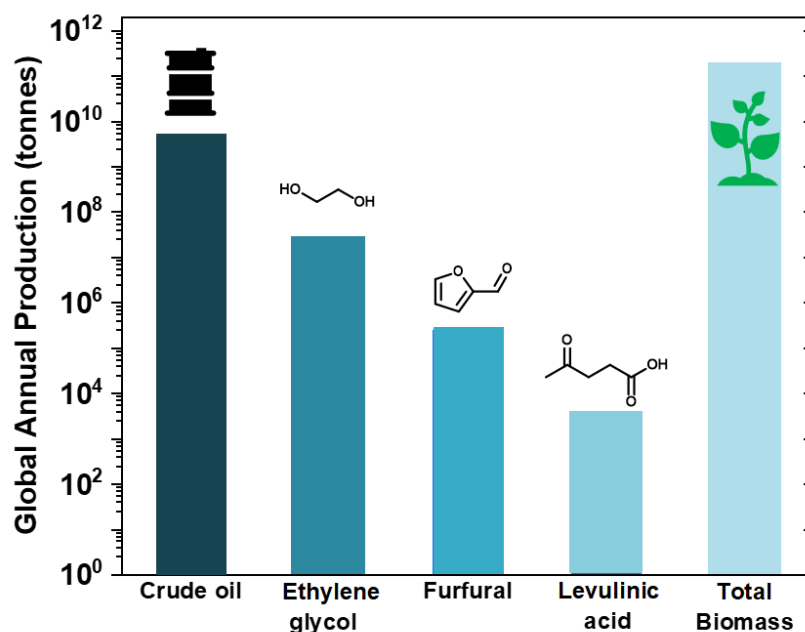


Figure 1.3.3. Annual production of biomass and crude oil feedstock, compared to annual production of the platform chemicals ethylene glycol (EG), furfural, and LA. Industrial HMF production is currently in its infancy and is limited. Data points were extracted from references.^{5,36,50,54,59}

1.4 CO₂ as a Platform Chemical?

A popular method for reducing CO₂ emissions in the atmosphere is to capture CO₂ emissions resulting from fossil fuel combustion to sequester them, through means such as storing them in carbonates or burying them under rocks or oceans.⁶⁰ However, the potential for a circular economy appears if one considers using CO₂ as a building block for useful fuels and chemicals. In this respect, rather than just storing the CO₂, it becomes advantageous to convert CO₂ emissions into higher-valued compounds such as ethylene or CO which can result in a circular economy (**Figure 1.4.1**). One metal which is of interest for the electrochemical CO₂ reduction reaction (CO₂RR) is copper, as it is the only reported monometallic species that can produce C₂₊ hydrocarbons and alcohols due to unique moderate binding energies for CO.⁶¹

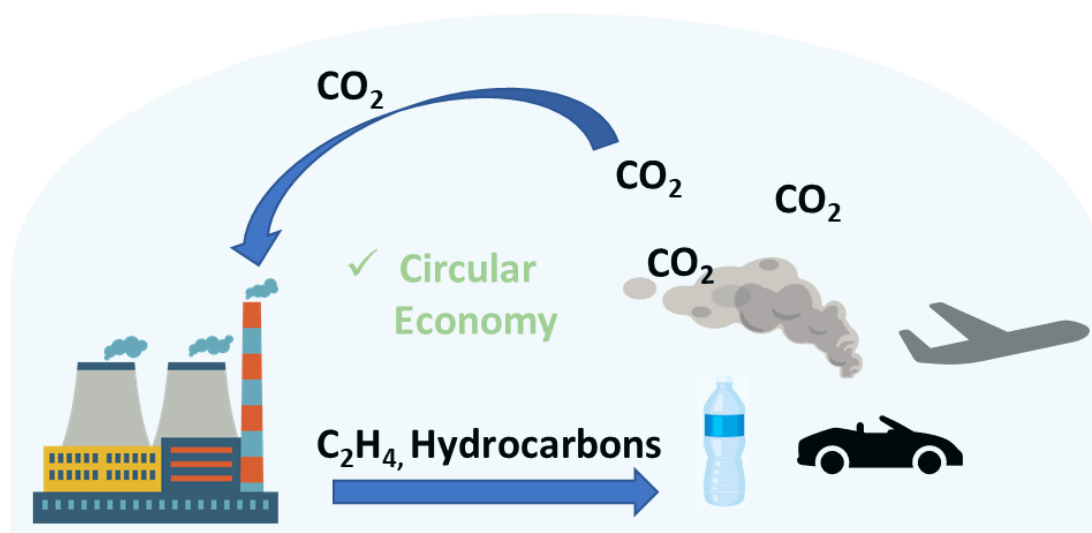


Figure 1.4.1. Example of a circular economy regarding carbon emissions. An ideal scenario would lead to CO_2 from vehicles and waste polymer incineration (in this case polyethylene) being captured and converted back into fuels or polymers.

Other catalysts which have been of interest for the CO_2RR are metal-organic frameworks such as single-atom porphyrins and phthalocyanines, which show great activity for electrochemically reducing CO_2 into syngas ($\text{CO} + \text{H}_2$) or purely CO .^{62,63} Other studies have synthesised metal single-atom catalysts on N-doped graphene for the same reaction.^{64,65} Iron single-atom metal-organic frameworks have been synthesised and characterised by Barrio et al.⁶⁵ for use in the oxygen reduction reaction. Nitrogen-coordinated single-atom catalysts have become popular with electrochemists in recent years, mainly for the CO_2RR and display favourable properties for use as electrocatalysts. These include:

- Reactions on these catalysts are assumed to take place only on the central metal atom. This provides well-defined active sites and almost a 100% atom economy,⁶⁶ which makes it simpler to calculate turnover frequencies by assuming each metal atom constitutes an active site.
- Alternative substrate binding modes are also possible on these sites compared to metal surfaces, i.e., they may only bind specific functional groups onto the central metal atom, distinct from the entire molecule binding on metal electrodes, which may have effects on product selectivity.
- The frameworks for these catalysts are made from cheap, ubiquitous elements C, H, O, and N. These catalysts are easily able to be modified with electron-donating and withdrawing groups which have been reported to have diverse effects on product selectivity during the electrochemical CO_2RR .^{67,68}

1.5 Nitrogenated Platform Chemicals

To widen the range of possible products from waste biomass, nitrogen moieties can also be introduced into platform chemicals.⁶⁹ Nitrogen-containing species are important building blocks that have uses in polymers, textiles, and even medicines.^{70,71} The carbohydrates which constitute lignocellulosic biomass do not contain any nitrogen moieties, so the incorporation of nitrogen requires an external nitrogen source (Figure 1.5.1). The presence of nitrogen moieties from natural feedstock is relatively limited, only appearing in food waste, proteins, polysaccharides such as chitin, and some forms of algae.⁷² Hydrothermal conversions of chitin have been shown to produce amines and *N*-heterocycles from crustacean shells – of which about 6-8 million metric tonnes are produced each year.⁷³ The composition of waste crustacean shells consists of chitin (15-40%), proteins (20-40%) and calcium carbonate, which can pose challenges to scientists in separating each component without much damage to proteins and chitin during the depolymerisation process.

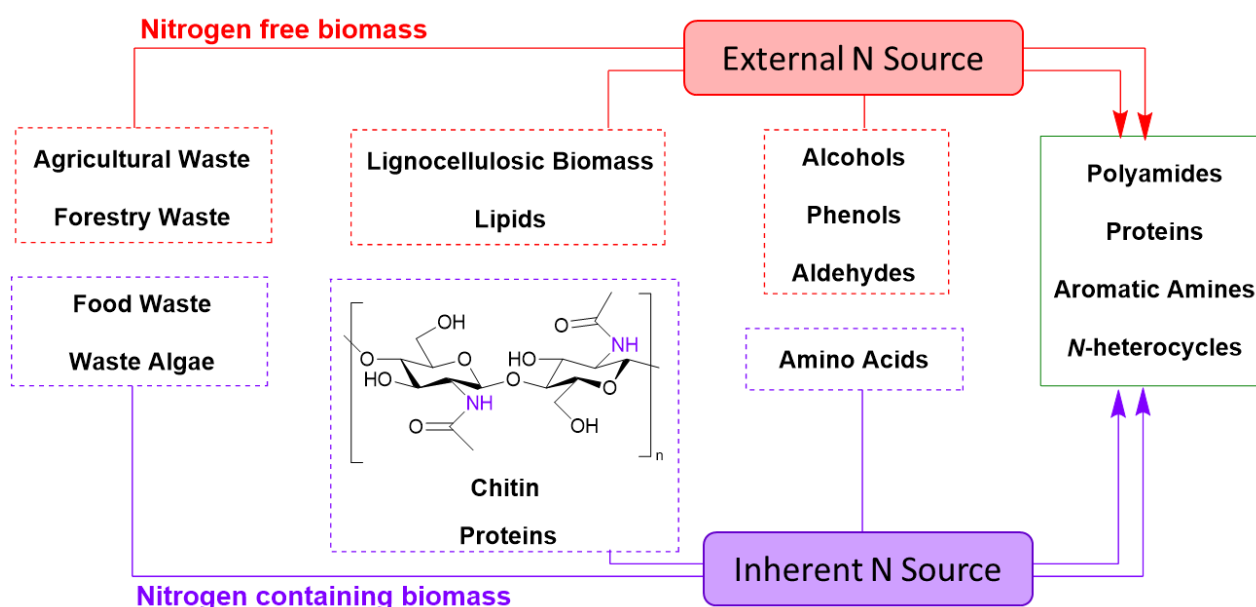


Figure 1.5.1. Production of useful aminated compounds from N-containing and non-N-containing biomass sources.

1.6 Electrochemistry vs Thermochemistry

Currently, in industry, most large-scale chemical syntheses occur using thermochemical methods which have noticeable drawbacks, such as the use of high temperatures, pressures, copious amounts of toxic solvent waste produced during synthesis and chromatographic purification, and the use of stoichiometric amounts of transition metal catalysts. For example, the industrial synthesis of TPA is done via the AMOCO process which entails the aerobic catalytic oxidation of *p*-xylene using cobalt or manganese catalysts in an acetic acid medium, between 175-225 °C at 15 – 30 bars of pressure.⁷⁴ In an article by Schiffer et al.,⁷⁵ the feasibility of thermal, mechanical, and electrical energies to drive chemical reactions are all compared. The authors conclude that using only thermodynamic data is insufficient to make conclusions from, and so other factors such as kinetics, costs, and associated unit operations such as separations must be considered. In the remit of green chemistry, it is possible to quantify these factors by calculating the process mass intensity (PMI, **equation 1.6.1**) of a synthesis, which can help evaluate the effectiveness of a green synthesis route.⁷⁶ The aim for green chemists is to keep the value of PMI as close to one as possible, however, today most thermochemical productions of chemicals have large PMIs.⁷⁶ To produce new efficient synthesis routes, we must aim to have processes with low PMI to make large-scale valorisation of biomass more attractive. Ways this can be achieved is to telescope multistep syntheses to reduce solvent-heavy purification steps and develop synthesis routes with high conversion percentages (**equation 1.6.2**).

$$\text{Process Mass Intensity (PMI)} = \frac{\text{Total mass used in a process (kg)}}{\text{Mass of product (kg)}} \quad \text{Eqn. 1.6.1}$$

$$\text{Conversion (\%)} = \frac{\text{moles of product made}}{\text{moles of biomass consumed}} \quad \text{Eqn. 1.6.2}$$

A cleaner alternative route to produce chemicals is through electrosynthesis, which will be defined as the electrochemical conversion of platform chemicals to produce higher valued compounds for the scope of this thesis. In brief, during electrosynthesis a constant electric potential or constant current can be held an electrode to oxidise or reduce targeted functional groups on platform chemicals. The applied potential should be as close to the equilibrium potential as possible to maximise efficiency. The equilibrium potential is the theoretical potential at which a reaction would proceed at equal rates in the forward and backward directions (no net current) on a perfect catalyst. In general, the equilibrium potential depends on the concentrations of the reactants and products according to the

Nernst equation (**equation 1.6.3**). Therefore, it is more common to use the standard equilibrium potential, which is the equilibrium potential under idealized conditions (activity=1 for all products and reactants). These can be calculated from tabulated standard Gibbs free energies of formation ($\Delta_f G^0$) but for an electrochemical reaction (**equation 1.6.4 & 1.6.5**). This requires a definition of the free energy of formation of an electron. For this, we define standard equilibrium to be with respect to the reversible hydrogen electrode, allowing us to set the free energy of formation of an electron plus a proton to be equal to zero (**equation 1.6.6**). The onset potential is an often arbitrarily used concept to describe the potential at which a reaction occurs at a measurable rate; for the purpose of this thesis, it is defined as the potential needed to achieve a 1 mA of current. The difference between the potential required to drive a specific current density and the equilibrium potential is known as the overpotential, which should be minimised for efficient electrochemical synthesis. Some of the equilibrium potentials for common HMF/furfural upgrading are depicted in **Figure 1.6.2** and are calculated from tabulated literature values of $\Delta_f G^0$ using the Nernst equation.⁷⁷

$$U_{eq} = U^0 - \frac{RT}{zF} \ln \left(\frac{[\text{products}]}{[\text{reactants}]} \right) \quad \text{Eqn. 1.6.3} \quad U^0 = -\frac{\Delta G^0}{zF} \quad \text{Eqn. 1.6.4}$$

$$\Delta G^0 = \sum \Delta_f G^0(\text{products}) - \sum \Delta_f G^0(\text{reactants}) \quad \text{Eqn. 1.6.5}$$

$$\Delta_f G^0(\text{H}^+ + \text{e}^-) = \Delta_f G^0(0.5 \text{ H}_2) = 0 \quad \text{Eqn. 1.6.6}$$

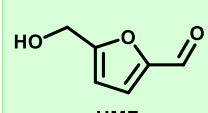
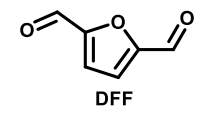
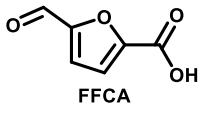
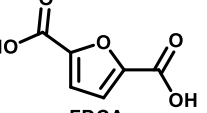
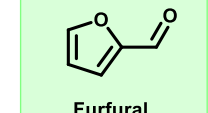
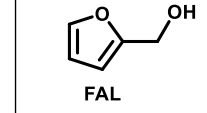
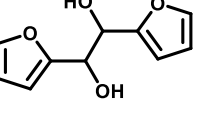
 Name Eq. Pot. n ^o e ⁻ (V vs RHE)	 HMF 0 N/A	 DFF -2 -1.29	 FFCA -4 -0.88	 FDCA -6 -0.45
	 Furfural 0 N/A	 FAL 2 0.19	 2-MF 4 0.34	 Hydrofuroin 2 0.21

Figure 1.6.2. Products available from HMF and furfural valorisation, along with their calculated equilibrium potentials. Values for $\Delta_f G^0$ taken from literature values for HMF oxidation products.⁷⁷ For furfural reduction products, the values for $\Delta_f G^0$ were calculated using density functional theory by Sihang Liu.

Electrochemistry can be used to develop synthesis processes which are less environmentally damaging and solves a lot of the problems associated with thermochemistry. These include:

Scalability – Industrial electrosynthesis does not require the large-scale infrastructure that thermochemical synthesis needs for operating at high temperatures and pressures.

Using electrons as a reactant – Electrons provide a clean reactant that can replace expensive noble metal catalysts. Using electrons provides versatility as they can be used as the reactant for many different reactions. In addition, electron transfers can occur rapidly under mild conditions, usually at room temperature, thus product selectivity can be controlled simply by using a specific applied potential.

Unstable reagents can be produced *in situ* without the risk of contamination – Traditional thermochemical methods may require the use of unstable reagents. Electrosynthesis can generate these only when they are required by oxidising or reducing a precursor, such as electrochemically producing unstable epoxides from alkenes.⁷⁸ In addition, the clean, non-toxic nature of electrons lowers the risk of reagent contamination. These advantages can contribute to safer chemical syntheses.

The use of green energy sources to provide electrons - The electricity required for synthesis can be directly connected to a renewable source such as wind or solar, meaning useful chemicals can be synthesised in great quantities without any greenhouse gas emissions.

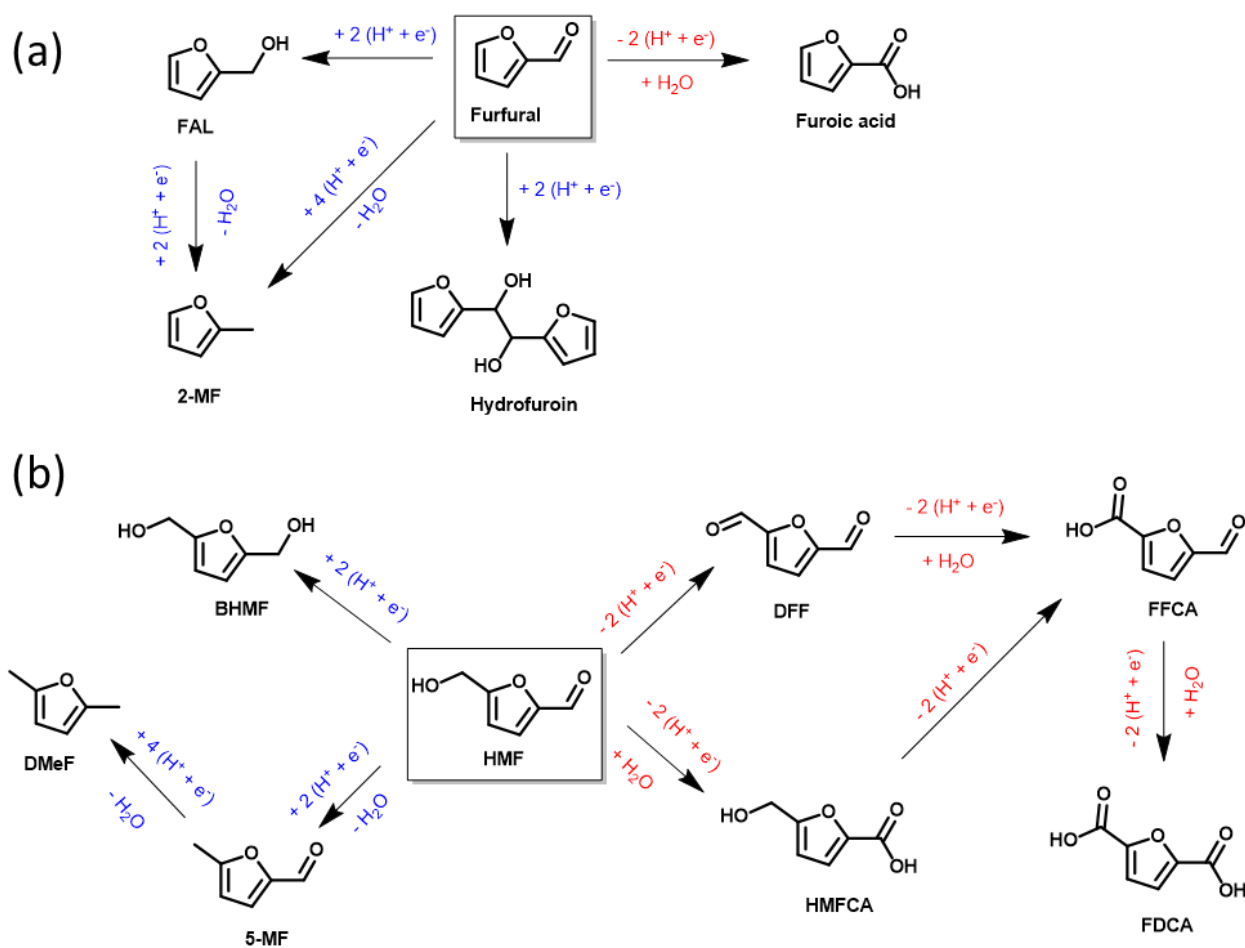
Small-scale electrochemical syntheses are usually done in a standard aqueous 'H' type electrochemical cell which contains three electrodes labelled as the working, counter, and reference electrode. The working electrode is usually the site of the focused biomass upgrading reaction whereas relatively inconsequential reactions occur at the counter electrode. By supplying an electric potential, it is possible to oxidise or reduce functional groups of platform chemicals on the surface of the working electrode. The measurement of an applied potential involves the reference electrode which has a known value that can be used as a reference point to measure the potential difference at the working electrode. In aqueous electrochemistry, potential values can be converted to the reversible hydrogen electrode (RHE) scale which is advantageous as this scale is independent of pH, making it easier to compare the electrochemical activity of different processes and is done using **equation 1.6.7**.

$$U_{\text{RHE}} = U_{\text{measured}} + U_{\text{reference}} + 0.059 \times \text{pH} \quad \text{Eqn. 1.6.7}$$

The efficiency of an electrochemical synthesis reaction is described as the Faradaic efficiency (FE) and is the ratio of the charge that is required to complete an electrochemical reaction compared to the total charge passed during the reaction. The equation for FE is given by **equation 1.6.8**, where n , F , z , and Q are the number of moles produced, Faraday constant (96485 C mol^{-1}), number of electrons transferred per mole, and total charge passed, respectively.

$$\text{Faradaic Efficiency (\%)} = \frac{n \times F \times z}{Q} \times 100 \quad \text{Eqn. 1.6.8}$$

The electrochemical valorisation of the platform chemicals mentioned previously can be broadly put into two main reaction types – electrochemical hydrogenation (ECH) and electrochemical oxidation reactions. **Scheme 1.6.1** shows the library of potential products available from electrochemical hydrogenation (blue labels) and electrochemical oxidation (red labels) of HMF and furfural along with the number of electrons required for the respective conversions.

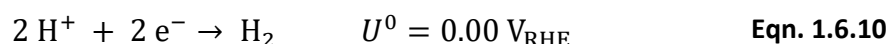


Scheme 1.6.1. Possible reduction and oxidation products available from (a) furfural and (b) HMF. Red labels depict electrochemical oxidation products and blue labels depict electrochemical hydrogenation products.

Electrochemical hydrogenation – Electrochemical hydrogenations of platform chemicals occur at the cathode and involve the reduction of an organic substrate via the addition of hydrogen using an applied cathodic potential. Water oxidation occurs at the counter electrode to produce protons and dioxygen. This counter-reaction is labelled as the oxygen evolution reaction (OER, **equation 1.6.9**). In an electrochemical cell, the source of hydrogen comes from water oxidation at the anode, with the resulting protons diffusing to the cathode to be used in reducing organic functional groups (**Figure 1.6.1**). The electrochemical hydrogenation of furanic compounds can yield useful solvents and biofuels such as 2-MF and DMeF but can also result in ring-opening reactions. At cathodic potentials, single-electron reductions are also possible which result in radical formation which can lead to electrochemical radical couplings to produce hydrofuroin which can be used as a precursor to drop-in jet-fuels.⁷⁹



Electrochemical Oxidation – These reactions involve the adsorption of a platform chemical on the anode surface, followed by the removal of electrons and protons from the initial molecule using an anodic potential, resulting in the formation of an oxidised version of the molecule. Primary alcohols are some of the most popular functional groups present in naturally occurring biomass and their oxidation can produce carboxylic acids, which are favourable functional groups for condensation polymers, highlighting the importance of these reactions in the electrochemical biorefinery. For electrochemical oxidation reactions, protons are reduced to produce dihydrogen at the counter electrode, during what is called the hydrogen evolution reaction (HER, **equation 1.6.10**).



Both reaction types have competing reactions which must be suppressed. At cathodes, the HER competes with biomass reduction to produce dihydrogen via a Volmer-Heyrovsky or Volmer-Tafel step (**Figure 1.6.1**). Whilst H_2 is a valuable product, its production during furfural electroreduction can have detrimental impacts on FEs because electrons that would ideally be consumed by furfural reduction, are used to reduce protons instead, and H_2 production could pose safety risks. This is a similar story for electrochemical oxidation reactions and the OER at the anode, however, another competing reaction is present here with regards to anode corrosion, because many electrode materials themselves can become oxidised at high anodic potentials which ends up corroding the anode.^{80,81} For example, graphene supported Ru anodes were reported by Huang et al.⁸² for the OER, which showed that Ru in fact catalysed the graphene support degradation into CO_2 . It is therefore paramount that electrosynthesis reactions are conducted at a potential where competing reactions are minimal. An

illustration of furfural electrovalorisation and the associated competing reactions involved are shown in **Figure 1.6.1**.

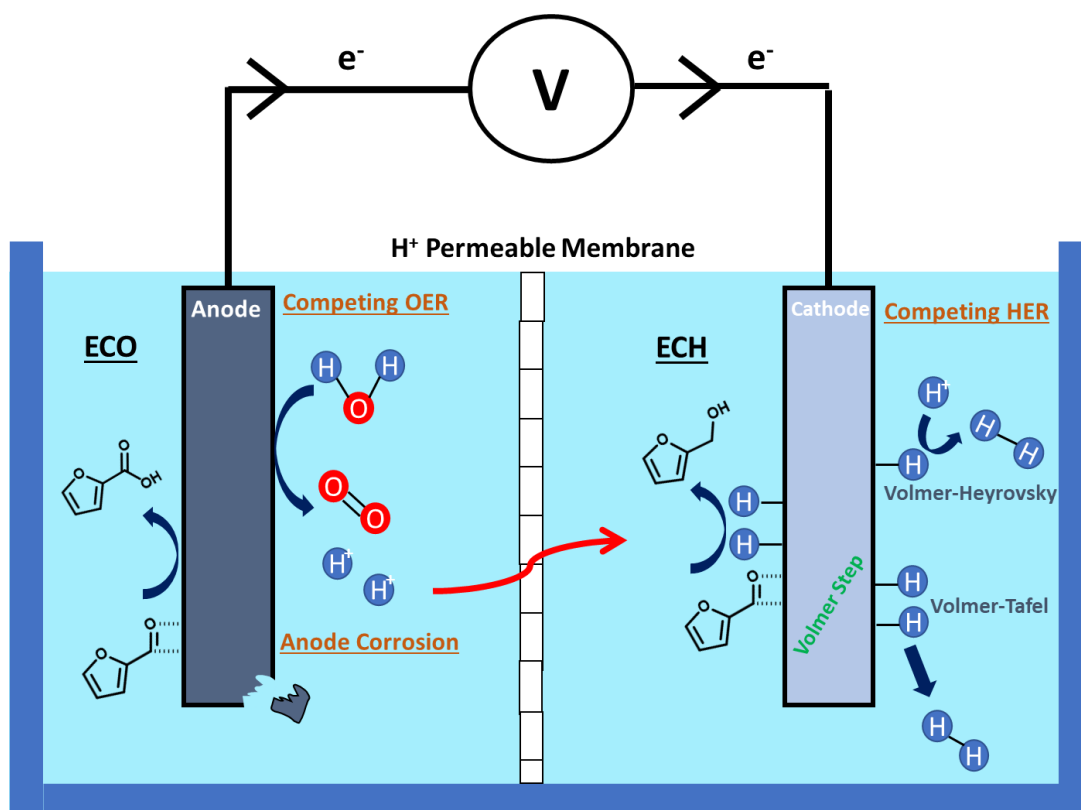


Figure 1.6.1. ECH and electrochemical oxidation (ECO) reactions of furfural occurring in an aqueous H-type electrochemical cell, depicting competing HER, OER, and anode corrosion competing reactions.

For industrial electrovalorisation to become feasible, a continuous synthesis is preferred over a batch process. A membrane electrode assembly (MEA) configuration provides an ideal system for continuous electrochemical synthesis as it can reduce mass transport limitations and can reach high current densities. The structure of these devices involves reactions at the anode and cathode being separated by a sulphonated polymer membrane such as Nafion™, intimately sandwiched between the two electrodes (**Figure 1.7.1**). MEA devices have been used previously for other electrochemical conversions including the CO₂RR,^{83,84} water electrolysis,⁸⁵ and hydrogen peroxide synthesis.⁸⁶ Reports for electrochemical upgrading using these devices on furanic compounds are much more limited so this presents an opportunity to set the agenda for industrial biomass upgrading. Some reports exist for the electrochemical oxidation of glycerol using an MEA device demonstrating current densities of up to 326.3 mA cm⁻² using 1 M initial glycerol concentration.⁸⁷

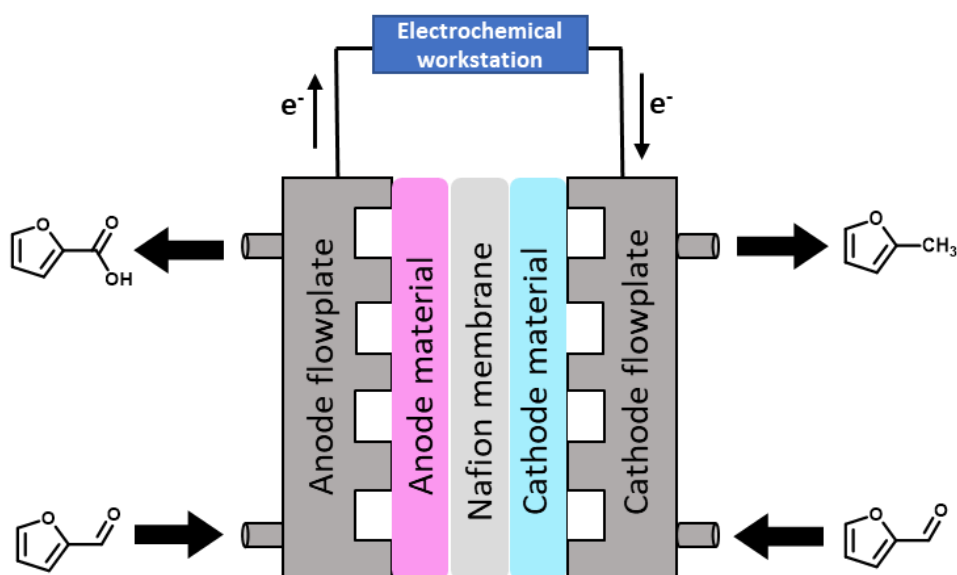


Figure 1.7.1. Illustration of typical zero gap MEA device which can be used for continuous biomass electrovalorisation.

When deciding the appropriate anode/cathode material, the Sabatier principle is an important concept at the heart of heterogeneous catalyst synthesis. It was first introduced by Nobel laureate Paul Sabatier in 1913 and stated that the binding between a catalyst and a substrate needs to be just right to ensure efficient reactions. If the binding energy is too weak, none of the adsorbates will bind to the catalyst surface, if too strong, products of the catalysis will fail to desorb and poison the catalyst surface.⁸⁸ During the mid-20th century, experimentally measurable parameters such as hydride formation⁸⁹ were used in place of binding energies as no direct methods to calculate binding energies existed. Over the last few decades, the widespread emergence of using density functional theory (DFT) has made calculating binding energies a routine process which in turn makes the Sabatier principle an effective predictive tool to synthesise new catalysts, with Nørskov and Rossmeissl making this quantitative for the HER and the oxygen reduction reaction.^{90,91} When choosing the best material for the working electrode, the activity of many electrodes for different reactions can be screened and activity can be plotted as a function of binding energy to find the optimal binding energy to guide material discovery (**Figure 1.7.2**).

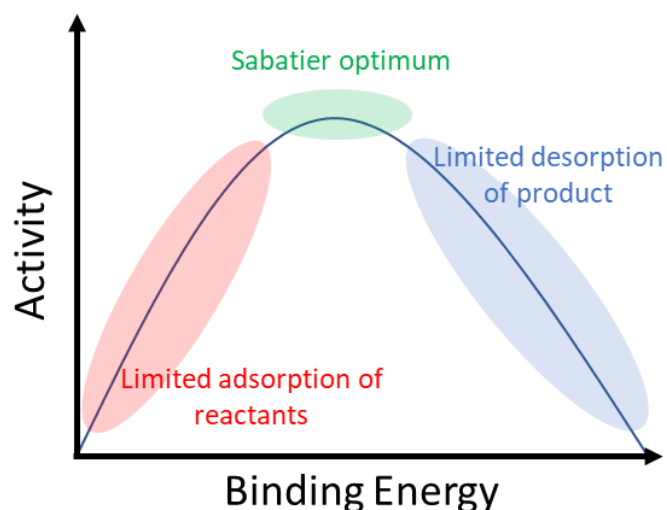


Figure 1.7.2. Example illustration of the Sabatier principle. The highest activity of an electrode is determined where adsorption and desorption energies are balanced. This is usually known as a ‘volcano’ plot.

Figure 1.7.3 shows the number of publications for the electrochemical conversion of furfural, HMF and levulinic acid. The number of publications is increasing exponentially over the last twenty years and is only predicted to increase further as we transition from a fossil fuel-based society to a more sustainable one. Most publications in the literature are demonstrated on a small scale; if we are to create a paradigm shift in the way we produce chemicals, we must assess whether it is possible to upscale these chemicals into larger continuous processes.

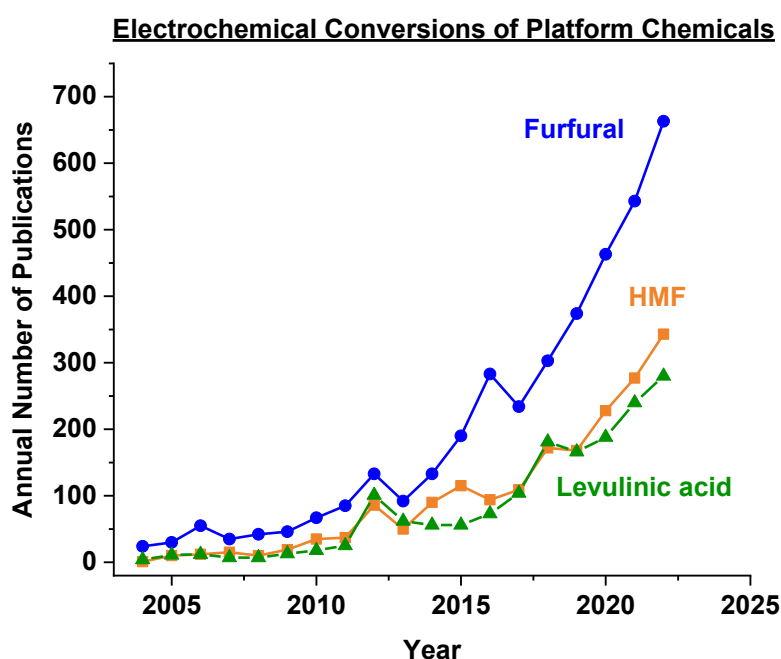


Figure 1.7.3. Publications on the electrochemical conversions of platform chemicals over the last few years. Numbers were obtained using the Scopus database.

2 | The Current State-of-the-art

In this section, the focus will be given to the electrochemical oxidation and reduction of the furanic platform chemicals, HMF and furfural. Useful information from publications surrounding the electrochemical conversion of said compounds is sorted into sections that will be organised according to the types of electrochemical reactions: reductions, oxidations, reductive aminations, and electrochemical ring openings. In addition to furanic compounds, the reported electrochemical upgrading of small aliphatic molecules such as EG and LA are also considered but to a lesser extent. Efforts will be made to see if the following questions can be answered in available literature, and if they are not, what further information is required to answer them. From this, it will be possible to pinpoint areas which need further work and will form the base for experimental projects:

- (1) What are the underlying properties of electrode materials that govern the ability of functional groups to undergo electrochemical hydrogenation, oxidation, ring opening, and reductive amination?
- (2) What is the effect of other reaction parameters such as pH, applied potential, and initial concentration of substrates on electrochemical synthesis?
- (3) What are the importance of non-electrochemical steps that need to be considered in these conversions e.g., nucleophilic addition steps or solution-based reactions between the platform chemical and the electrolyte?

2.1 Electrochemical Reduction Reactions

The reduction of furfural produces chemicals such as FAL, 2-MF, and hydrofuroin, as well as their fully hydrogenated derivatives if the furan ring is reduced. However, the extra thermodynamic stability of the furan ring makes the complete reduction of these compounds unfavourable under ambient conditions⁹² and has only been reported in small amounts (8% FE for 2-MeTHF) on Pd electrodes at high overpotentials.⁹³ Hence, for this review, we will only focus on the reduction of the substituted functional groups. In general, platform chemicals with multiple oxidation/reduction products can have their selectivity and reaction efficiency governed by a combination of the electrode material, solvent composition, salt composition, electrolyte pH, applied potential, and the initial concentration of the biomass feedstock, which all need to be optimised for an efficient synthesis.⁹⁴ **Figure 2.1.1** shows a comparison of the electrochemical selectivity of various metal electrodes for furfural reduction. Whilst the number of electrodes which can produce FAL is diverse, the production of hydrofuroin is limited to Al, Hg, Pb, and Cd electrodes, and for 2-MF only Cu electrodes have been reported to produce 2-MF with selectivities above 80% FE.

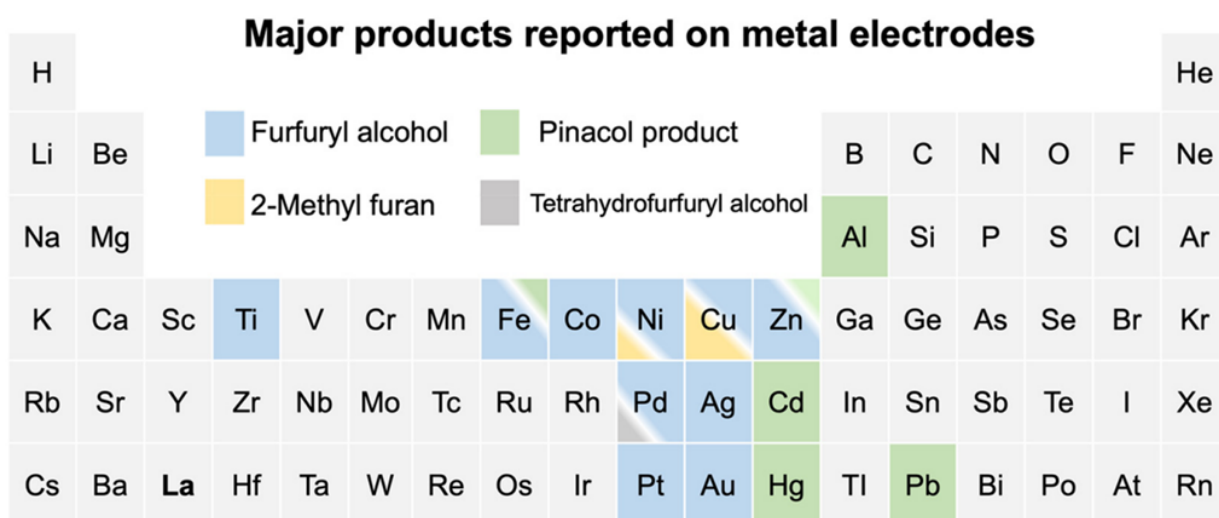


Figure 2.1.1. Summary of major reported furfural electrochemical reduction products on monometallic electrodes at moderate cathodic potentials. The ratio of the shaded squares depicts the major and minor products. The pinacol product represents hydrofuroin. Cu electrodes are the only monometallic species which produce 2-MF with high FEs. The figure was produced by myself and Sihang Liu from our recently published peer-reviewed paper,⁹⁵ with data points taken from other references.^{96–105}

2.1.1 Factors Governing Furfural Reduction Selectivity

Whilst Nilges and Schroeder⁹⁶ have reported up to 28% FE for 2-MF production on Ni electrodes, Cu electrodes are the present state-of-the-art for 2-MF production and report FEs of over 80% and high current densities at relatively low operating potentials (-0.50 to -0.75 V vs RHE).⁹⁶ This is advantageous as Cu is a cheap transition metal and is relatively abundant. For electrochemical hydrofuroin production, the best-reported electrodes are carbon and Pb which have shown between 60-70% FE at mild cathodic potentials.⁹⁶ The effect of the electrode material on selectivity can be rationalised by a Sabatier principle type relationship that relates the relative binding affinities between an organic substrate and the electrode surface and hydrogen.¹⁰⁶ In brief, we can come to an initial observation that if a surface binds hydrogen too strongly, the HER will likely dominate, whereas weaker hydrogen binding may prevent surface-level hydrogenation altogether leading to radical coupling, and a balance between the two can result in more effective electrochemical reductions i.e. for 2-MF selectivity. This is roughly outlined in (Figure 2.1.1.1), which shows the LSVs of reported Pb, C, Cu, and Pd electrodes, showing the major products obtained on the relevant electrodes, in acidic electrolyte. It is important to reacknowledge that selectivity can be governed by a combination of parameters, for example, Pb electrodes have been demonstrated to produce 2-MF at very cathodic overpotentials in acidic media.¹⁰⁷

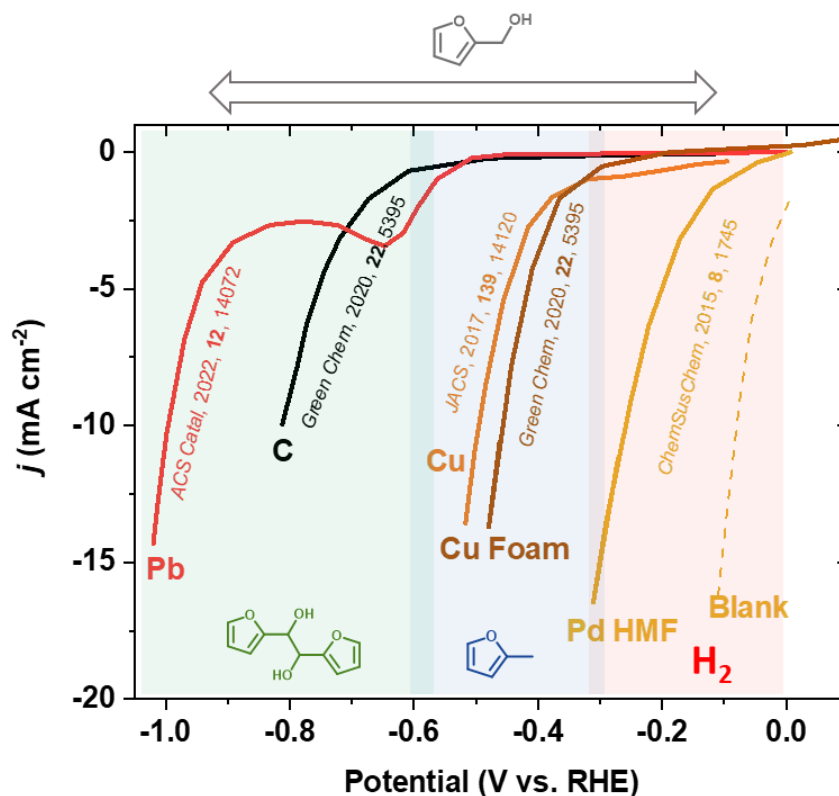


Figure 2.1.1.1. Co-plotted linear sweep voltammograms of different metal cathodes for the electrochemical reduction of furfural or HMF. Shaded areas depict major furfural reduction productions reported.^{79,107–109}

The pH of the electrolyte is an important parameter which can be tuned to target specific reduction products. For 2-MF production, an acidic electrolyte is a necessity on Cu, which was proven by Liu et al.¹¹⁰ by conducting furfural reduction in pH 10 and only seeing FAL as the main product with over 70% FE. At low pH, the competing HER is more active compared to in alkaline electrolytes which is depicted in **Figure 2.1.1.2**, where it is seen that HMF hydrogenation and HER tend to have similar onset potentials at low pH.¹¹¹ There is a greater difference in the onset potentials between HER and HMF reduction at neutral/basic pH but in acidic pH, the onset potentials of the HER and of HMF electroreduction are less cathodic than when compared to neutral media. It is also worth noting that the activity of HER is greater at low pH. An explanation for this was suggested whereby the activation barrier for HER is lower at this pH.¹¹² At a higher pH, there is a lower concentration of H^+ and in turn a lower chance of inducing unwanted HER steps. From this, it is possible to hypothesise that running the electrochemical reduction reactions at basic pH could be one possible option to suppress the HER and increase overall reduction efficiency.

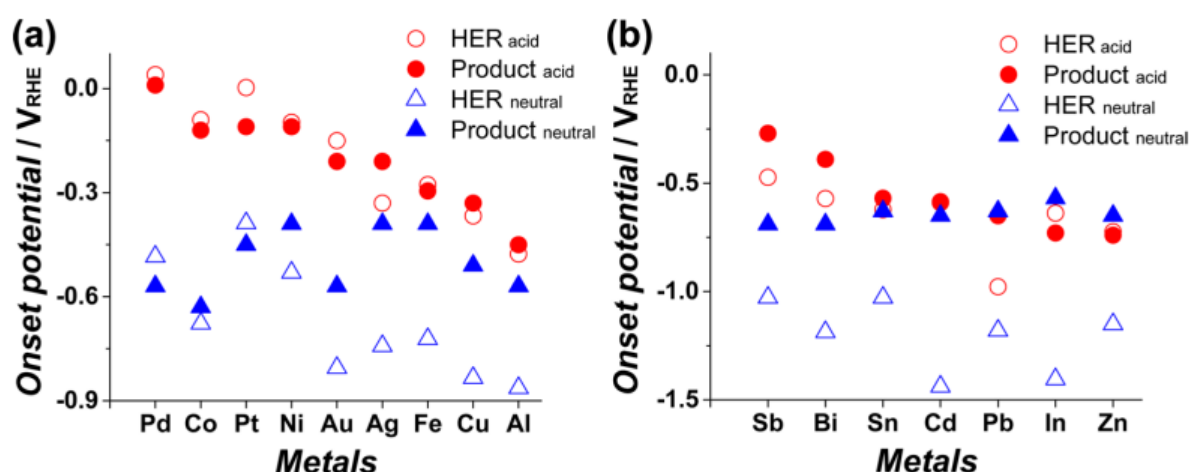


Figure 2.1.1.2. Comparison of the onset potentials of (a) transition metals and (b) post-transition metals with regards to the HER and HMF reduction, in acidic (0.5 M H_2SO_4) and neutral (pH 7 phosphate buffer) media. Onset potentials of HER were reported at a current density of -0.5 mA cm^{-2} . Figure reprinted with permission from publisher.¹¹¹

The effect of acidic pH on 2-MF production was seen on Cu electrodes by Jung and Biddinger,¹¹³ whereby electrochemical furfural reduction was tested in 0.1 M NH_4Cl (pH 3.4), 0.1 M H_2SO_4 (pH 1.1), and 0.5 M H_2SO_4 (pH 0.5), at a constant current density of -10 mA cm^{-2} . 2-MF had the highest FE at pH 0.5 (31%) and decreased as the pH increased, with less than 2% FE of 2-MF being recorded at pH 3.4.¹¹³ The authors also saw this effect using different concentrations of HCl, which suggested that this effect

was due to pH and not the nature of the anion.¹¹³ In contrast, the selectivity for FAL increased significantly when the pH was raised to between pH 6-10. This was also seen by Brosnahan et al.¹¹⁴ whilst studying furfural reduction using Ag₆₀Pd₄₀ nanoparticles. To selectively produce FAL, a neutral pH was optimal due to lower onset potentials for furfural reduction, and low amounts of HER in these conditions compared to other electrolytes, namely the acidic electrolytes which showed increased levels of HER. Interestingly, neutral K⁺ and Na⁺ phosphate buffers showed no difference in FAL selectivity. Whilst no explanation for this was given, it is useful to know that the choice of cation is a parameter which affects product selectivity in the CO₂RR.^{115,116}

The initial concentration of furfural is another factor which was shown to play a role in controlling the selectivity of furfural reduction products by Jung et al.¹¹⁷ in acidic media (0.5 M H₂SO₄). At low initial furfural concentrations, H₂ gas was the main product, and the combined FAL and 2-MF Faradaic efficiency increases with increasing starting concentrations of furfural, alongside decreasing HER rates (Figure 2.1.1.3). Humins, which are oligomers produced during furfural degradation, were formed at high concentrations which was also seen by Parpot et al.¹¹⁸ in 0.1 M KOH (pH 13) solution at high concentrations of furfural on Cu electrodes. They also witnessed that by increasing the initial concentration from 0.25 to 0.50 M, the total yield of furanic products decreased by 27%.

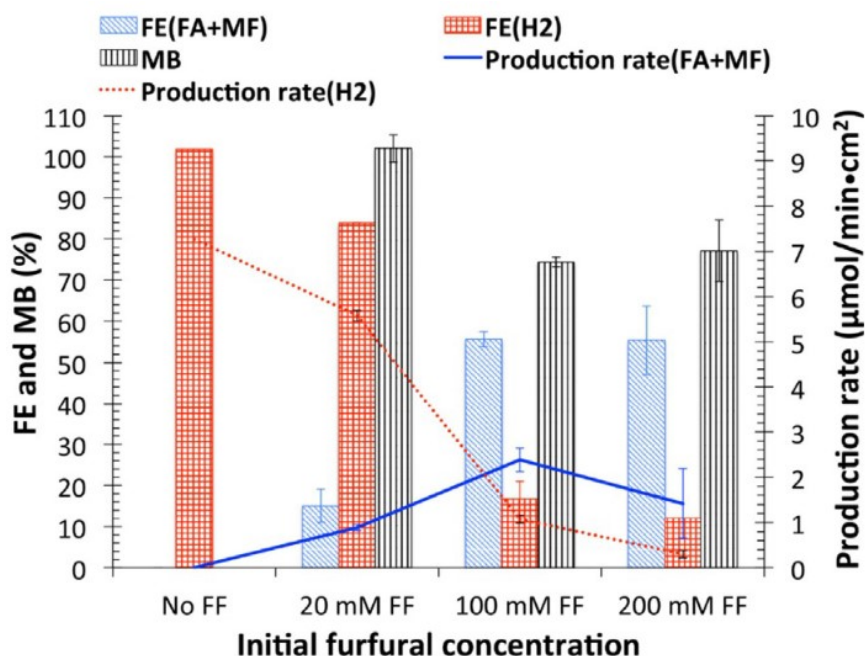


Figure 2.1.1.3. Products from electrochemical furfural reduction with changing initial furfural concentration. Reaction conditions: 0.5 M H₂SO₄ electrolyte with 4:1 ratio of acid to acetonitrile co-solvent, Cu foil electrode, 1.5 h reaction time at -0.80 V vs RHE. Abbreviation: MB = mole balance, FA = furfuryl alcohol, MF = 2-methylfuran. Figure reprinted with permission from publisher.¹¹⁷

Raman studies were used by Li and Kornienko¹¹⁹ to study furfural reduction on different Cu facets (111, 110, 100, and roughened Cu), at -0.526 V vs RHE in acidic electrolyte. The study concluded that the Cu(110) surface produced FAL with the highest FE (up to 80%), whereas the roughened Cu exhibited 2-MF as the major product. The authors explained this result due to the increased number of defects in the roughened surface providing binding sites for a CH₂OH group to adsorb, straining the bond, and making it easier to cleave off.

A general qualitative representation for furfural reduction on Cu was produced by May and Biddinger (**Figure 2.1.1.4**) depicting the expected products which should be produced under certain parameters.⁹⁴ Although the qualitative representations are from experimental results in their group, it could be possible that some general trends can be used to explain or possibly predict results on other electrodes. For example, the humin products at very high initial furfural concentrations may be independent of electrode materials, due to the general instability of furfural, especially in alkaline pH.

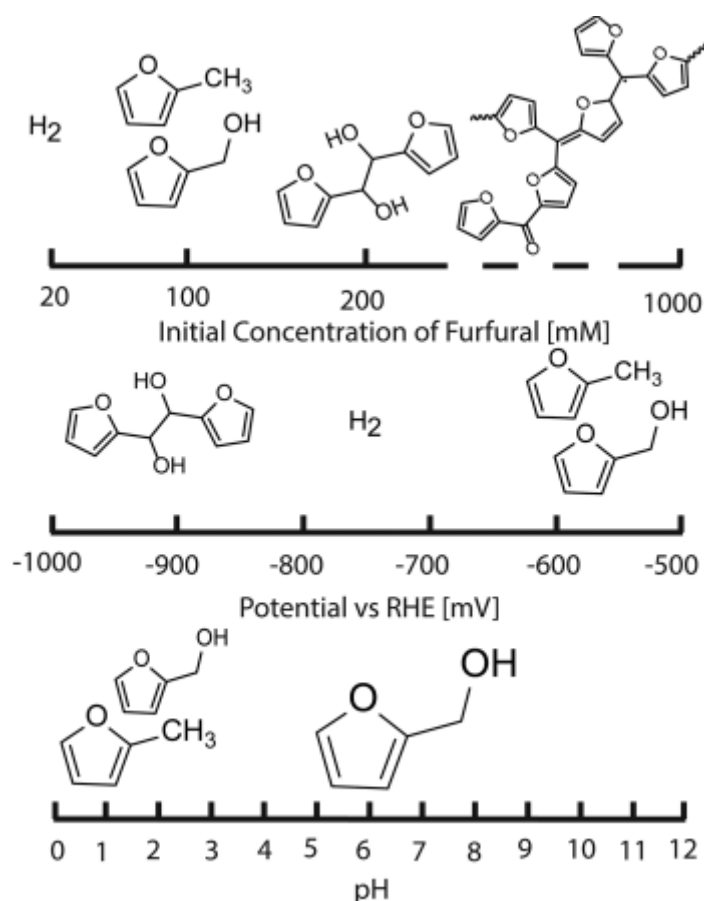


Figure 2.1.1.4. Qualitative selectivity predictions of furfural reduction products on Cu electrodes. The size of the molecules represents the relative abundance expected for each parameter. Figure reprinted with permission from publisher.⁹⁴

Understanding the mechanisms behind electrochemical reduction reactions provides us with invaluable information which can help to produce more selective electrochemical synthesis processes in the future. For furfural reduction, these can be separated into two categories – carbonyl bond reduction to form FAL and 2-MF, and radical coupling to produce hydrofuroin.

Carbonyl bond reduction – Following the adsorption of furfural, two possible mechanisms for reduction are possible which include a direct reduction of the carbonyl bond using adsorbed hydrogens (ECH mechanism), or a proton-coupled electron transfer (PCET) using H^+ ions in solution (electroreduction mechanism). An electrochemical hydrodeoxygenation (HDO) is also possible and can remove oxygen atoms on furfural as water. Work from Chadderdon and co-workers¹⁰⁸ suggested two possible pathways of electrochemical carbonyl reduction in aqueous media on Cu electrodes (**Figure 2.1.1.5**). The authors suggested an outer-sphere pathway where parts of the reduction do not occur on the electrode surface in the case of direct electroreduction (blue pathway, **Figure 2.1.1.5**) and an inner-sphere pathway whereby the reduction of the carbonyl group is achieved completely on the electrode surface using adsorbed hydrogens (red pathway, **Figure 2.1.1.5**).

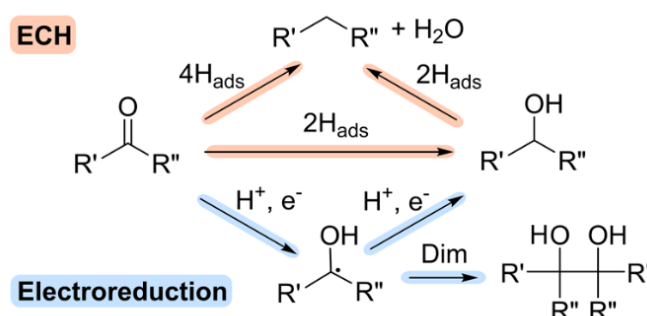


Figure 2.1.1.5. Proposed electrochemical reduction pathways of carbonyl compounds. The red pathway depicts the ECH pathway using adsorbed hydrogens, whereas the blue pathway depicts the PCET pathway. Figure reprinted with permission from reference.¹⁰⁸

Reductive Radical Coupling – The proposed outer-sphere electroreduction mechanism (blue pathway, **Figure 2.1.1.5**) shows the potential for producing radical species which can self-dimerise to produce a pinacol product. This is a possible method of producing C-C bonds under mild conditions in contrast to popular methods of thermochemical C-C couplings done via expensive Pd-catalysed Suzuki¹²⁰ or Stille reactions.¹²¹ By coupling two furfural molecules together, hydrofuroin can be produced which is attracting attention as a potential drop-in jet fuel once it undergoes further reduction, usually by using Pd/C and H_2 gas to produce straight chain hydrocarbons.⁷⁹ The mechanism of hydrofuroin production from furfural was studied by Chadderdon and co-workers by covering the

surface of Cu electrodes with self-assembled monolayers (SAMs),¹⁰⁸ to essentially prevent hydrogen surface adsorption, essentially blocking the ECH route. This led to only hydrofuroin being produced suggesting the production route is primarily an outer sphere mechanism (**Figure 2.1.1.6**).

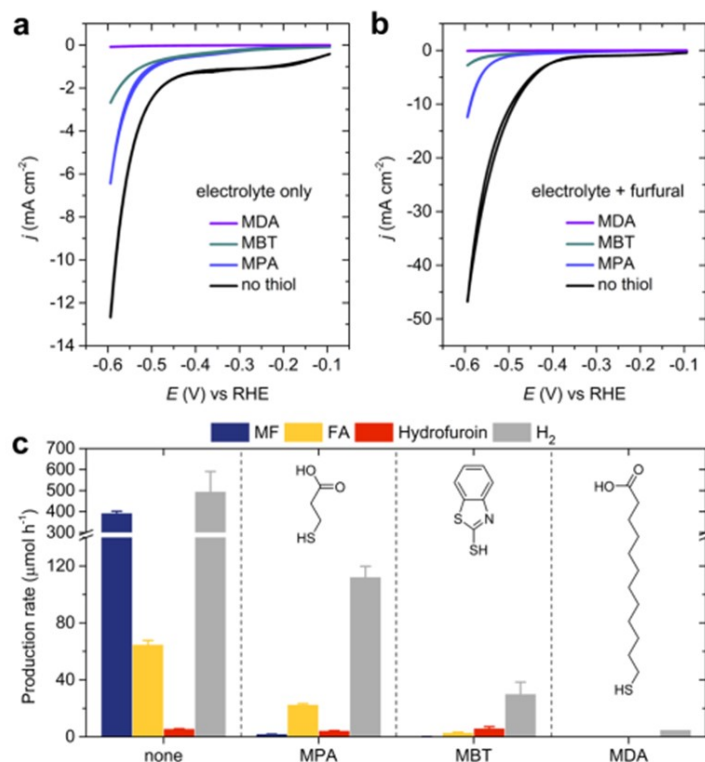


Figure 2.1.1.6. (a) Cyclic voltammograms (CVs) of a Cu rotating disc electrode (RDE), with and without the addition of various SAMs on the Cu surface. (b) CVs of the same surfaces after the addition of 0.05 M furfural. (c) Recorded production rates on Cu, Cu-MPA, Cu-MBT and Cu-MDA electrodes. Reaction conditions: pH 0.5 H₂SO₄ electrolyte, 0.25 mM organothiol SAMs, and 0.05 M furfural. The potential applied was -0.55 V (vs RHE). Abbreviations: MDA – 12-mercaptododecanoic acid, MPA – 3-mercaptopropionic acid, MBT – 2-mercaptobenzothiazole. Figure reprinted with permission from publisher.¹⁰⁸

Electrochemical furfural reduction on Pb, Al, and carbon electrodes was studied by Nilges and Schroeder⁹⁶; they reported greater selectivity towards hydrofuroin than Cu. Chadderdon et al.¹⁰⁸ also reported results for furfural reduction on Pb electrodes in acidic electrolyte with about 30% FE for hydrofuroin, but there were many unidentifiable products which were attributed to unselective radical coupling to form oligomers that can poison the electrode. It was further suggested that the furfuryl radicals coupled on the electrode surface without the use of adsorbed hydrogens, as Pb has a notoriously large overpotential for HER due to H binding very weakly on this surface.¹²² This was in contrast to a study by Lie et al.¹⁰⁷ whereby a combination of electron paramagnetic resonance (EPR) spectroscopy and theoretical techniques, identified the furfuryl radical in the electrolyte solution on Pb electrodes in acidic pH. This conclusion suggests that there may be a secondary mechanism for

electrochemical reductive coupling reactions, however further detailed literature on solution coupling mechanism was limited.

Surface level radical coupling of benzaldehyde was probed using Raman studies by Anibal et al.¹²³ who were able to detect benzyl radical formation on Pt, Pd and Au surfaces. Although the radical was detected, the main product on these electrodes was benzyl alcohol, as opposed to the coupled product, which suggests that radical formation may not always result in coupling products and that other factors influence selectivity. A similar result was also seen by Lopez-Ruiz et al.¹²⁴ using different metal electrodes were able to produce a volcano plot (**Figure 2.1.1.7**) showing Pd as the best-performing catalyst for benzyl alcohol production. Similarly, none of the coupled products were seen using platinum group metals (Pd, Pt, Ni). Anibal et al.¹²³ highlighted the stability of the ketyl radical on the electrode surface as an explanation, as well as suggesting a smaller concentration of ketyl radicals favours reduction into alcohols as there are no radicals in proximity for them to couple with. The radical was most stable on Cu compared to other metals explaining the increased coupling products seen on Cu.¹²³ Lopez-Ruiz et al.¹²⁴ suggested that platinum group metals require adsorbed hydrogens for sufficient reduction activity. Another explanation was suggested whereby the reduction activity on Pd may be explained by Pd being a hydride donor under cathodic conditions.¹²⁵ Surface poisoning of electrodes by Anibal et al.¹²³ using CO drew similarities towards the experiments by Chadderdon and co-workers¹⁰⁸ and rationalised the low coupling activity on Pt and Pd because of strong CO binding, likely poisoning the surface, compared to very little of this on Cu.

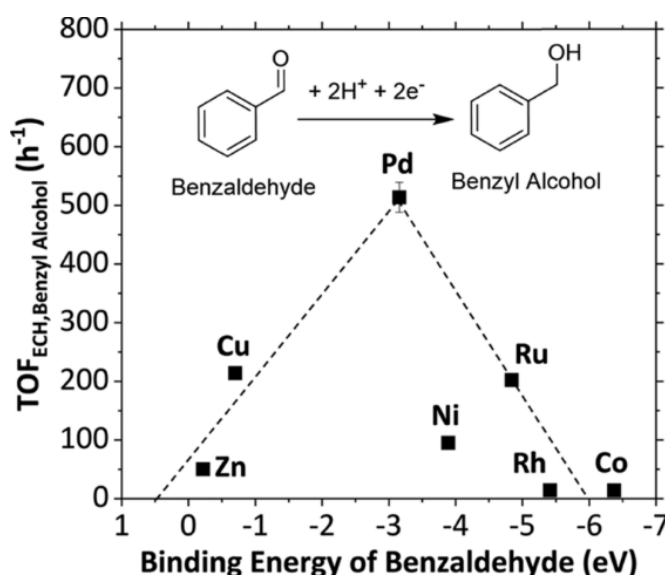


Figure 2.1.1.7. Volcano plot of experimentally obtained intrinsic electrochemical hydrogenation rates in the presence of benzaldehyde, with computed binding energies on different electrode surfaces. Electrolyte used was 47.5 % isopropanol, 47.5 % H₂O, and 5 % acetic acid, with 80 mM benzaldehyde at -1150 mV vs Ag/AgCl. Figure reprinted with permission from publisher.¹²⁴

Conductive carbon materials as electrodes are attractive options for electrodes because carbon is cheap and ubiquitous in nature. The dimerisation of HMF was seen on carbon electrodes by Kloth et al.¹²⁶ in alkaline electrolyte which produced the coupled species 5,5'-bis(hydroxymethyl)hydrofuroin (BHH) with FEs between 32-35%, but the other 65-68% of consumed HMF were unidentifiable products. This result was also seen in similar experiments of HMF electroreduction on carbon electrodes by Chadderdon and co-workers¹²⁷ where over 50% of the consumed HMF was also unidentifiable. Both authors suggested it was likely that unselective radical coupling occurred which produced oligomers after the single electron transfer to produce the radical in the first step. Other carbon-containing materials were also reported in this study including an experiment using Ag/C cathodes.¹²⁷ Whilst the main product detected was the diol BHMF, some experiments reported that BHMF made up only about 50% of the total product distribution, with the rest being unidentifiable. Whilst it could be argued the unidentifiable humins are from the Ag, it cannot be ruled out that secondary mechanisms occur on the carbon material which produces BHMF and oligomer products.

The rationale behind electrochemical radical coupling was extended further by Anibal and Xu¹²⁸ who attempted the heterocoupling of two aldehydes (furfural and benzaldehyde) on Pb electrodes in a near-neutral electrolyte. A maximum FE of 38% at $-0.60\text{ V}_{\text{RHE}}$ of the heterocoupled product was observed, with the rest of the products being the homocoupled hydrofuroin or hydrobenzoin. The effect of applied potential on selectivity was seen when at more cathodic potentials, the rate of radical coupling decreased and the aldehyde reduction into alcohols was the dominant reaction (**Figure 2.1.1.8**). Electrochemical cross-coupling between furfural and levulinic acid was also demonstrated by Wu et al.¹²⁹ but at an anodic potential of $1.41\text{ V}_{\text{RHE}}$, using Ni_3N particles in alkaline media. A selectivity of 80% of the coupled product was recorded at this potential.

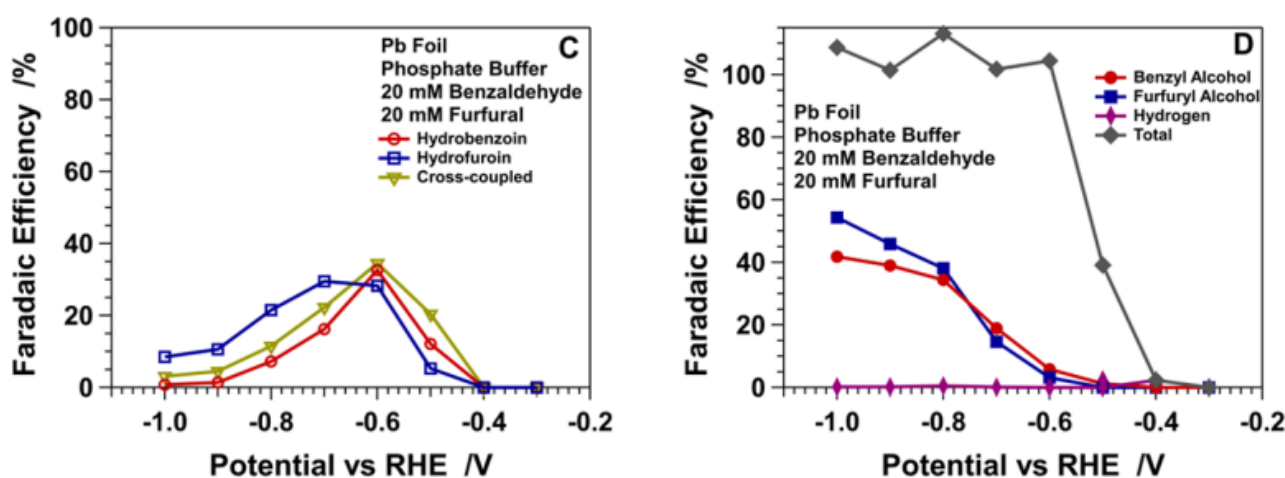


Figure 2.1.1.8. Electrochemical reduction of furfural and benzaldehyde on Pb foil. FEs of (left) coupled products and (right) reduced alcohol products after electrolysis. Reaction conditions: 0.25 M sodium phosphate buffer (pH 6.7), 20 mM of hydrofuroin and benzaldehyde.¹²⁸

Bondue and Koper¹³⁰ suggested that not only does the electrode material affect selectivity, but also the structure of the organic substrate can have significant effects on electrochemical reduction activity. By detecting the electrochemical reduction products of acetone, acetophenone, and 4-acetylpyridine, it was observed that Pt(111) and Pt(100) surfaces were unable to hydrogenate acetone but were able to hydrogenate acetophenone. This was attributed to the inability of Pt(111) and Pt(100) to bind acetone effectively, preventing adsorbed hydrogens from getting in close proximity to reduce the carbonyl bond. However, successful reduction was observed with acetophenone attributed to the horizontal adsorption of the aromatic ring on the Pt surfaces bringing the adsorbed hydrogens in proximity for hydrogenation. Interestingly, no reduction activity was observed with 4-acetylpyridine which was explained by the molecule adsorbing onto the electrode via the nitrogen atom of the pyridine ring, resulting in a vertical geometry, hindering electron transfer as the carbonyl group is not in proximity of adsorbed hydrogens on the electrode surface (**Figure 2.1.1.9**). A similar trend was seen by Lopez-Ruiz et al.¹²⁴ who showed that substrates with an aromatic ring displayed much higher activity than their straight-chain counterparts.

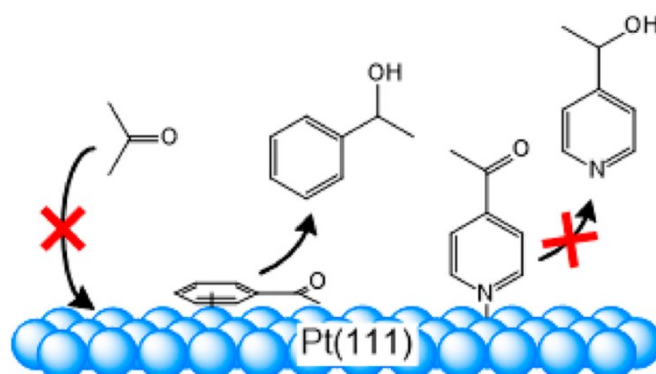
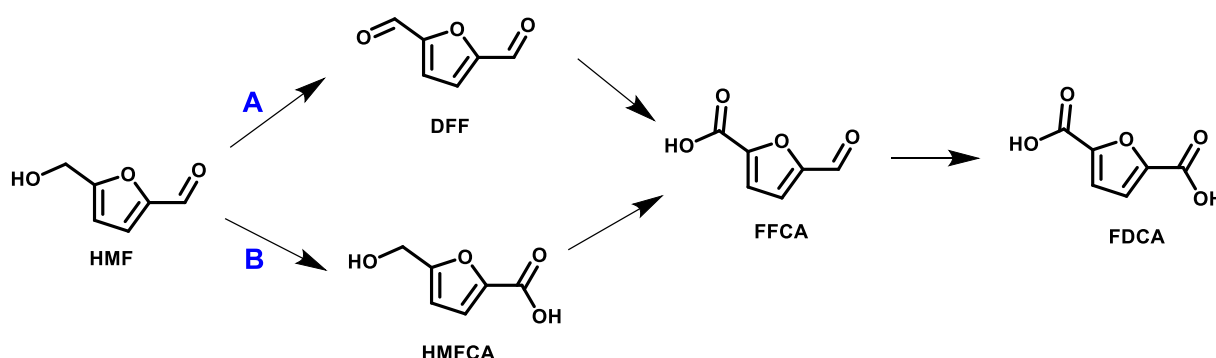


Figure 2.1.1.9. Proposed binding modes of acetone, acetophenone and 4-acetylpyridine on Pt(111) electrode. A correct binding geometry is needed for efficient reduction to be feasible, with the presence of an aromatic ring required for efficient electrochemical reduction.¹³⁰

2.2 Electrochemical Oxidation Reactions

A new library of products is available from the electrochemical oxidation of HMF using anodic potentials, which can produce the HMF oxidation products: DFF, HMFCFA, FFCA, and FDCA (**Scheme 2.2.1**). The electrochemical oxidation of furfural is generally less considered in the literature, likely due to the greater usefulness and prices of HMF oxidation products compared to furfural oxidation products. It is for this reason; this section will mainly focus on the electrochemical oxidation of HMF. Like electrochemical reduction reactions, the electrode material and the pH of the electrolyte can affect the selectivity and activity of oxidation reactions.¹³¹ For electrochemical alcohol oxidation, the preference for alkaline electrolytes was highlighted by Kwon et al.¹³² who reported that the first step of the reaction is an outer-sphere base-catalysed deprotonation to produce a reactive alkoxide species. In this regard, for ethanol oxidation on Au electrodes, the oxidation activity was orders of magnitude higher in pH 13 than that of acidic pH, supporting this notion.¹³²



Scheme 2.2.1. Competing pathways for HMF oxidation into FDCA.

The disubstituted nature of HMF results in two competing oxidation pathways (**Scheme 2.2.1**), which adds an extra layer of complexity in controlling selectivity. The choice of electrode materials can be a major factor in determining which route HMF oxidation products takes. HMF electrooxidation was reported as early as 1991 by Grabowski et al.¹³³ using Ni/NiOOH foam electrodes in 1 M NaOH electrolyte (pH 14), reporting a 71% product yield for FDCA production, with current densities as high as 16 mA cm⁻² and 84% FE. Other anode materials such as oxyhydroxides consisting of NiOOH, CoOOH and FeOOH were also reported for HMF oxidation activity by Taitt et al.¹³⁴ where it was seen that NiOOH films were the most efficient catalyst with reported FDCA selectivity and FE at 96% in a 0.1 M KOH electrolyte (pH 13). Latsuzbaia and co-workers¹³⁵ tested NiOOH foams for a continuous, industrial scale-up of HMF oxidation and reported high selectivity (90%) and FE (80%) for FDCA at pH 12. As

FDCA is insoluble in acid, a pH shift was able to separate FDCA from the electrolyte solution and was filtered off (**Figure 2.2.1**). As mentioned earlier in this thesis, the company Avantium⁴⁸ aims to commercialise this to produce large-scale FDCA production but has recently paused its production.

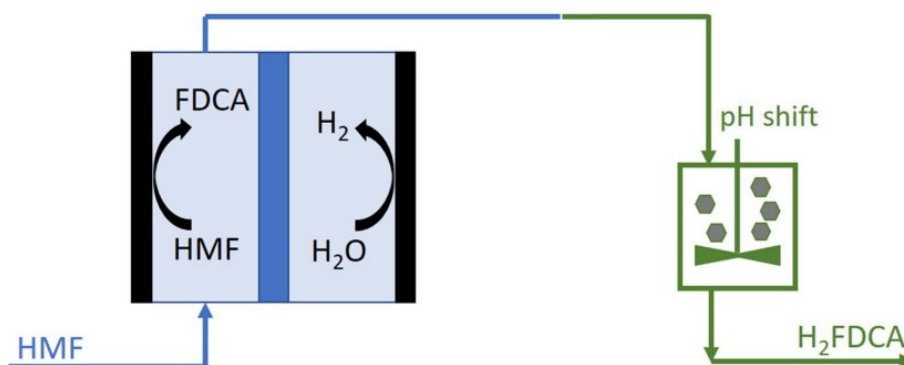


Figure 2.2.1. Large scale production and extraction of FDCA from HMF proposed by Latsuzbaia et al.¹³⁵ Figure reprinted with permission from publisher.

Whilst Ni-based catalysts are the present state-of-the-art for HMF electrooxidation, a study by Vuyyuru et al.¹³⁶ attempted to oxidise HMF on Pt electrodes, which produced DFF at 18% FE as the main organic product. Pt electrodes exhibit some HMF oxidation activity at low pH whereby it was reported a 4% yield of DFF was obtained at 2.0 V vs RHE in a pH 1.06 electrolyte.¹³⁵ The remaining ~96% of HMF consumed was unaccounted for and was labelled as HMF degradation products. This result was also seen by Kubota et al.¹³⁷ whereby DFF was produced at just 8% FE on Pt electrodes at acidic pH, with large amounts of HMF being consumed yet unaccounted for during quantification. One compound that was detected from this HMF degradation was maleic acid, which is a precursor to succinic acid – a dicarboxylic acid that can be used in renewable polymers.¹³⁸ The same study also used a MnO_x anode at 60 °C, to achieve FDCA at an impressive FE of 53.8% at 1.60 V vs RHE.¹³⁷ The synthesised FDCA spontaneously precipitated in the electrolyte due to the insolubility of FDCA in acidic media. This spontaneous precipitation of FDCA is useful because it negates the need for a reagent-heavy pH shift that would be required if an alkaline electrolyte was used (**Figure 2.2.2**). It is worth mentioning however, many electrodes are generally unstable in acidic media and quickly degrade above 1.30 V vs RHE.¹³⁹ The authors annealed the MnO_x electrodes at 400 °C for 2 h to improve chemical stability, although long-term electrode stability after electrolysis was not reported.

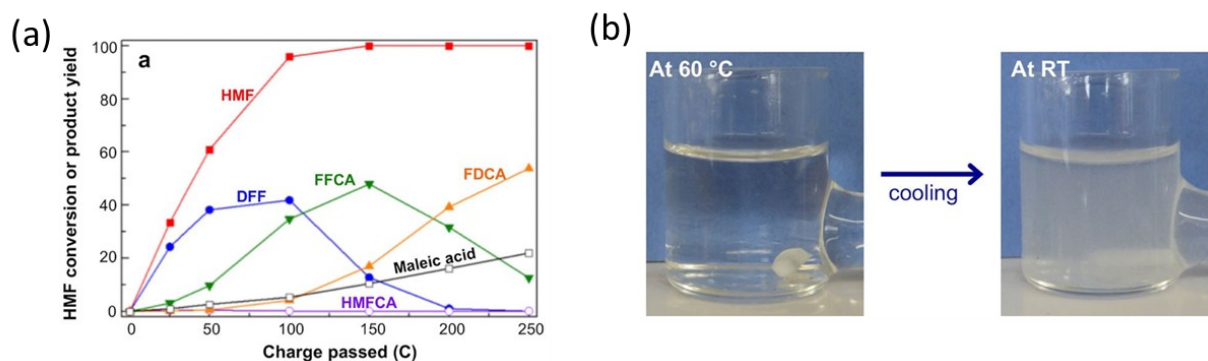


Figure 2.2.2. The electrochemical oxidation of HMF in acidic electrolyte at 1.60 V vs RHE using MnO_x electrodes. (a) Products obtained from HMF oxidation at different amounts of charge passed. (b) Precipitation of FDCA in solution after cooling from 60 °C. Figure reprinted with permission from publisher.¹³⁷

As well as electrochemical degradation, non-electrochemical HMF degradation into humin products is also an issue. HMF is a relatively unstable aldehyde which rapidly degrades into humin products without any catalyst or applied potential. Van Zandvoort et al.¹⁴⁰ reported that humin products form through condensation reactions between the aldehyde group of one HMF molecule and the beta position of the furan ring of another. Other mechanisms of humin formation exist including by Lund et al.¹⁴¹ suggesting a series of aldol condensations lead to the spontaneous production of humins. This is problematic as these oligomers can poison the electrode surface preventing oxidation activity. It is important to mention that the aldehyde group in HMF is non-enolisable and consequently makes HMF susceptible to the Cannizzaro reaction at high pH. This is a disproportionation reaction that occurs when two aldehydes react with each other in an alkaline solution (**Figure 2.2.3**). Studies on the Cannizzaro reaction of HMF in different alkaline solutions show that HMF is converted into FFCA and BHMF, as well as some humin products.¹⁴² As an alkaline electrolyte is preferred for oxidation, the Cannizzaro reaction and humin formation is difficult to avoid completely but may be minimised by using electrodes which rapidly oxidise HMF into more stable products or find a method which avoids using alkaline electrolytes.

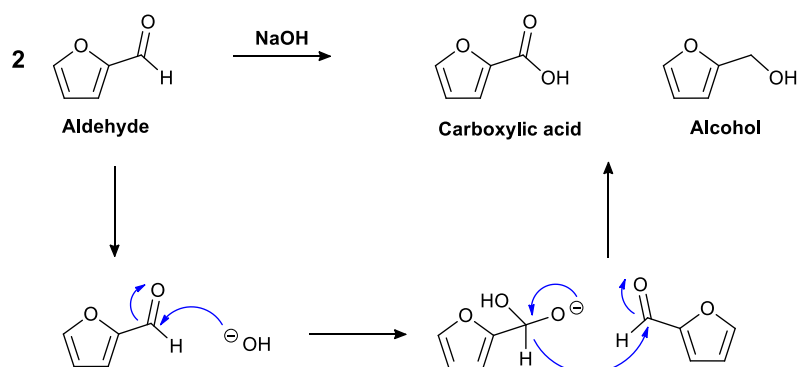


Figure 2.2.3. Mechanism for the base catalysed Cannizzaro reaction starting from furfural.

Other materials that were reported for electrochemical HMF oxidation are bimetallic Pd_xAu_y nanoparticles. A study by Chadderdon et al.¹⁴³ reported electrochemical FDCA production with FEs as high as 83% in alkaline media using Pd_1Au_2 anodes at 0.90 V vs RHE (**Figure 2.2.4**). It was suggested that Au and Pd nanoparticles on carbon are favourable for aldehyde and alcohol oxidation respectively, hence the complete oxidation on Au/C and Pd/C electrodes required a higher potential for oxidation activity (1.20 V vs RHE). When combined in a ratio of Pd_1Au_2 , a synergistic effect can produce FDCA at lower potentials with high FDCA selectivity. A similar conclusion was reached by Kim et al.¹⁴⁴ whereby Au/C anodes were deemed to be selective for aldehyde oxidation and would form HMFCA as the main product. The authors are adamant that this is the only step possible on Au/C cathodes, however, a work by Heidary and Kornienko¹⁴⁵ using operando Raman techniques concluded that DFF was the main product and not HMF. Au_3Pd_2 bimetallic species were also tested by Latsuzbaia et al.¹³⁵ with noticeable differences in electrochemical activity. Similarities remained with regards to high FE (84%) and selectivity (92%) for FDCA production however, a decrease in current density from 3.00 to 0.07 mA cm^{-2} was seen after 6 h at 1.15 V vs RHE, most likely due to Au poisoning, which was not reported by the previous study. The authors attribute this difference to the advantages of Au_xPd_y nanoparticles used by Chadderdon and co-workers as opposed to flat electrodes and wires, as well as using a higher pH of 13 as opposed to 12 in their study. The electrochemical activity was able to be regained after a pulse for 1 s at 2.0 V vs RHE which likely delaminated the poisoning off the electrode. It is not a surprise to see Au being poisoned under these conditions as a separate study on glycerol oxidation using Au in $\text{pH} > 13$, also reports a decrease in electrochemical activity over time due to a high amount of adsorbed hydroxide groups preventing adsorption of the biomass substrate.¹⁴⁶

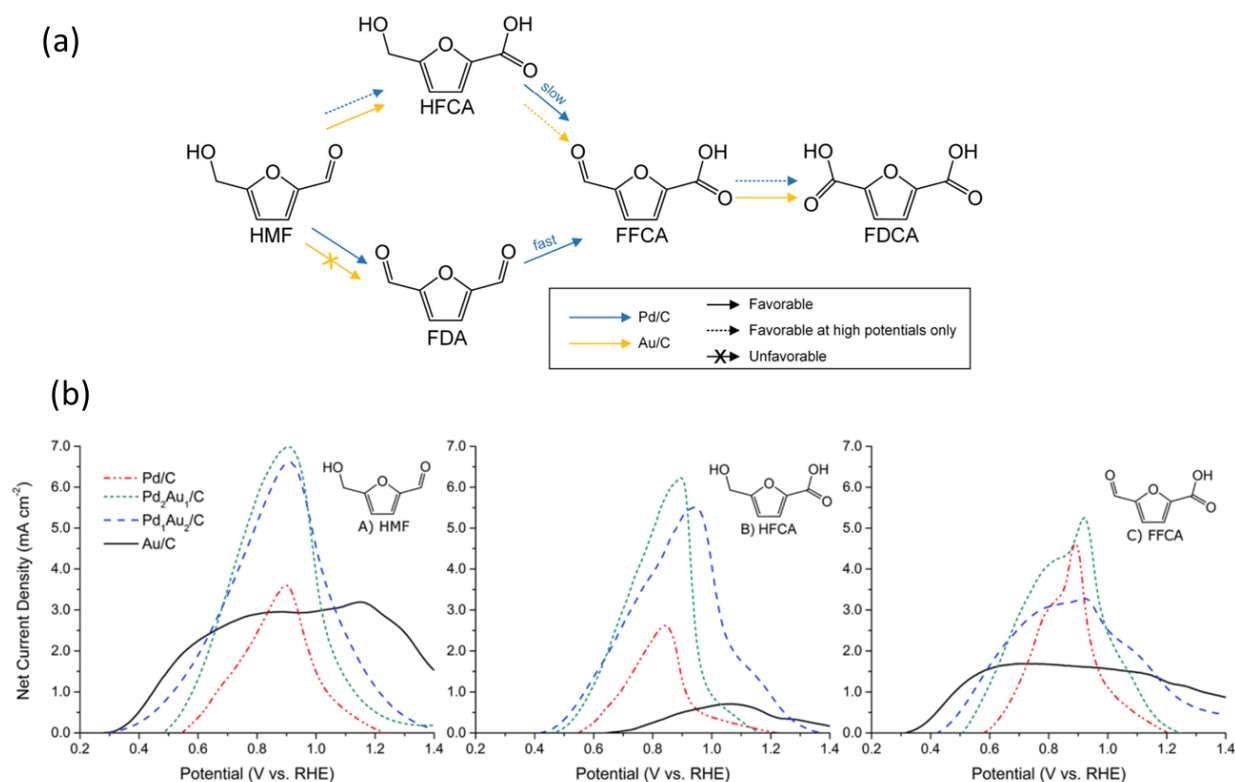


Figure 2.2.4. Electrochemical oxidation of HMF on Au_xPd_y electrodes. (a) Reported favoured reaction routes of HMF oxidation on Au/C and Pd/C anodes. (b) LSVs of various Pd and Au anodes using different starting substrates HMF, HMFA, and FFCA.¹⁴⁷

Whilst displaying high FEs, the price and limited supply of Pt, Pd, and Au, can make future commercial scale-ups of FDCA production problematic. Alternatives to the state-of-the-art NiOOH catalysts were studied exploring other metal oxyhydroxides. In a work by Taitt et al.¹³⁴ CoOOH displayed the lowest overpotential for HMF oxidation compared to Fe and Ni analogues which was attributed to a lower potential needed for the $M(OH)_2 \rightarrow MOOH$ conversion, however, the rate at which this happened was too sluggish to generate high current densities for constant potential experiments. Furthermore, FeOOH reported no activity before water oxidation potentials. The intrinsic activity of Ni and Co/CoO_x was explored by Heidary and Kornienko¹⁴⁸ using *operando* surface-enhanced Raman spectroscopy in highly alkaline media (1 M KOH, pH 14). From this study, it was seen that pH had a significant effect on selectivity as only DFF was seen in pH 12, compared to HMFA in pH 14, and further into FDCA at more anodic potentials. It was explained that due to lower concentrations of OH⁻ at pH 12, it becomes more difficult to nucleophilically oxidise the aldehyde into a hydrate, hence the lone alcohol is the only moiety which can be oxidised to produce DFF (**Figure 2.2.5**). At higher pH, this is not an issue and hence HMFA can be produced at lower overpotentials, however, the lone alcohol oxidation is suppressed which the authors showed using Raman studies. FDCA is rapidly formed at more anodic

potentials as the Ni/NiOH₂ is converted into the active Ni/NiOOH species, which can bind alcohol groups much better than the Ni/NiOH₂ precursor and is seen to readily oxidise both aldehyde and alcohol species on HMF.

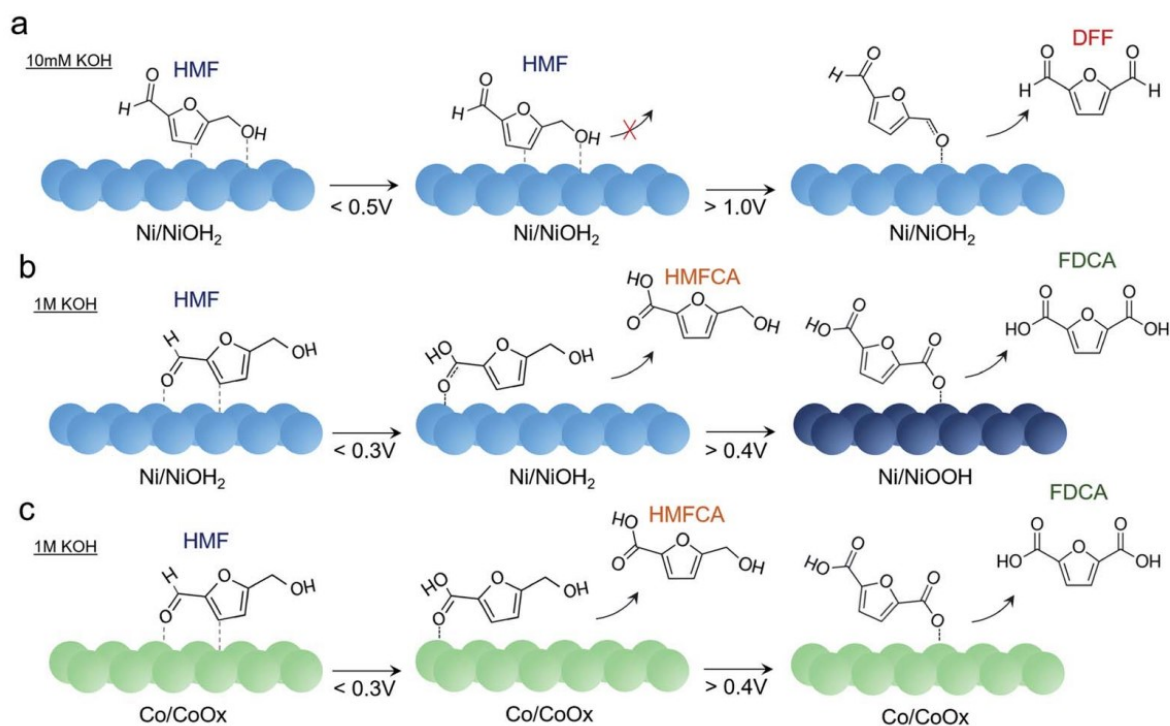


Figure 2.2.5. Proposed reaction HMF electrochemical oxidation pathways on Ni anodes in (a) 10 mM KOH, (b) 1 M KOH, and (c) on Co anodes in 1 M KOH. Figure reprinted with permission from publisher.¹⁴⁸

Although Co/CoO_x displayed disappointing HMF oxidation activity, Lu et al.¹⁴⁹ reported Co-based spinel oxides (Co₃O₄, ZnCo₂O₄) displaying FDCA production with FEs of over 90%, and current densities reaching 16 mA cm⁻², with currents as high as 60 mA cm⁻² when the spinel oxides are placed on Ni foam supports.

Metal-free catalysts for electrochemical oxidation reactions can be prepared from ubiquitous elements such as carbon, oxygen, nitrogen, and hydrogen. These include molecular catalysts such as the stable nitroxyl radical 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO). An applied potential oxidises TEMPO into the oxoammonium cation (TEMPO⁺), which facilitates the addition of an alcohol for further reduction. The TEMPO radical can then be restored electrochemically to complete the oxidation cycle (**Figure 2.2.6**). Cardiel et al.¹⁵⁰ reported the conversion of HMF into FDCA using TEMPO in a homogenous borate buffer solution (pH 9.2) and produced FDCA with 96.7% FE at 1.60 V vs RHE. Inductive effects were explored using 4-acetyl-TEMPO (ACT) which resulted in FDCA being produced

at a faster rate than TEMPO. It was suggested that the electron-withdrawing acetyl group quickly forms the active oxoammonium species, which results in a more anodic potential required to form the active TEMPO^+ species. The low price, high activity, low toxicity, and high FDCA yields obtained using TEMPO make this catalyst appealing for a scale-up of FDCA production. However, in this study TEMPO was in a homogenous solution, and will need to be separated from FDCA, likely requiring reagent-heavy chromatography methods. This step can be avoided by finding ways to immobilise TEMPO onto an electrode surface for use in heterogeneous electrocatalysis.

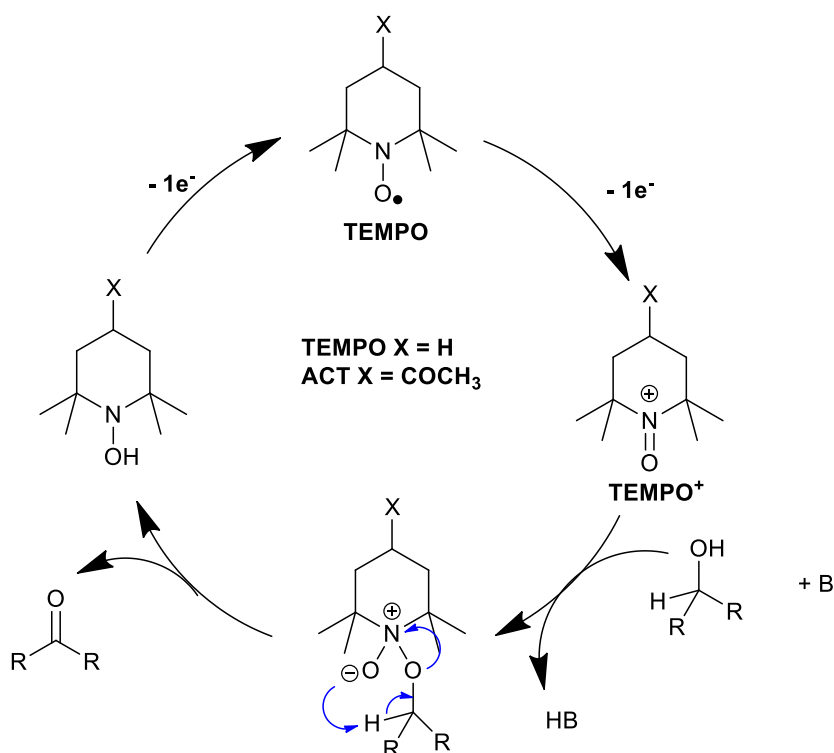


Figure 2.2.6. Electrochemical catalytic cycle of TEMPO demonstrating alcohol oxidation into aldehydes.

One immobilisation strategy for TEMPO was reported by Hickey et al.¹⁵¹ using covalent linkages between TEMPO and carbon chains to produce linear poly(ethylenimine) films (LPEI). The catalyst was used to oxidise several bioavailable alcohol-containing molecules including sucrose, methanol, and glycerol, displaying superior performances when compared to TEMPO in homogenous solutions, even after 24 h highlighting good stability. The catalyst was able to oxidise methanol into formaldehyde, which was further oxidised into formate and later into CO_2 (**Figure 2.2.7**). Noticeably, a higher current density was seen for CO_2 production compared to formaldehyde oxidation which was attributed to the aldehyde needing to be first hydrated to form an OH group which adds on the oxoammonium.

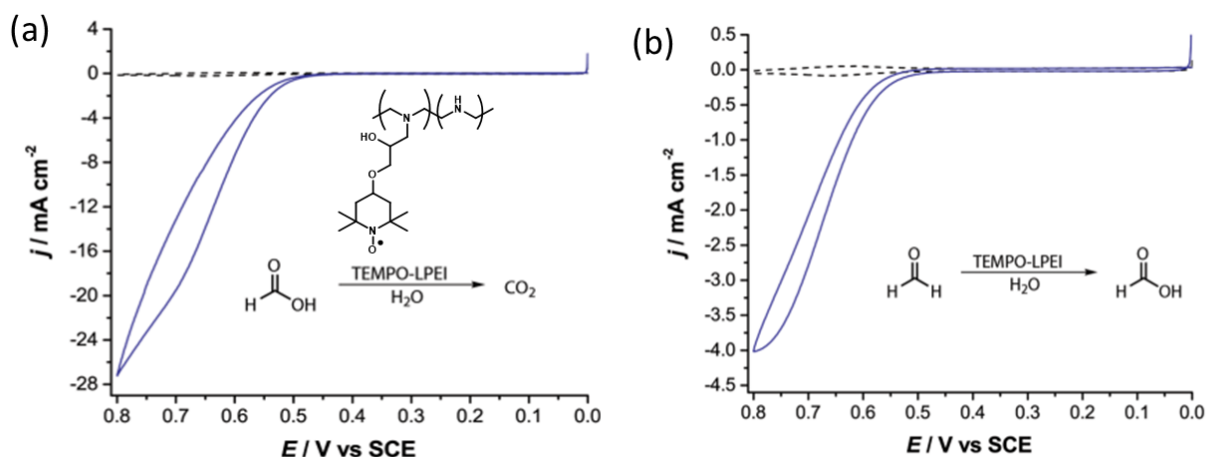


Figure 2.2.7. CVs of electrochemical oxidation of (a) formic acid and (b) formaldehyde using TEMPO-LPEI films before (dashed line) and after (solid line) biomass addition. Reaction conditions: 0.15 M phosphate buffer (pH 7), 0.5 M biomass, 10 mV s⁻¹ scan rate. Figure reprinted with permission from publisher.¹⁵¹

Non-covalent methods of TEMPO immobilisation have also been reported including attaching TEMPO moieties onto a cobalt phthalocyanine molecule (CoPc-TEMPO, **Figure 2.2.8a**), which π - π stacked onto a carbon electrode to minimise delamination.¹⁵² This compound was able to selectively oxidise benzyl alcohol into benzaldehyde with 85% FE in a 0.3 M carbonate buffer (pH 10), with no further oxidation into benzoic acid being detected. Another non-covalent method for TEMPO immobilisation was explored using pyrene-TEMPO by Das and Stahl (**Figure 2.2.8b**)¹⁵³ Similarly to the CoPc-TEMPO, benzaldehyde was the major product detected after electrochemical benzyl alcohol oxidation in a pH 10 electrolyte.

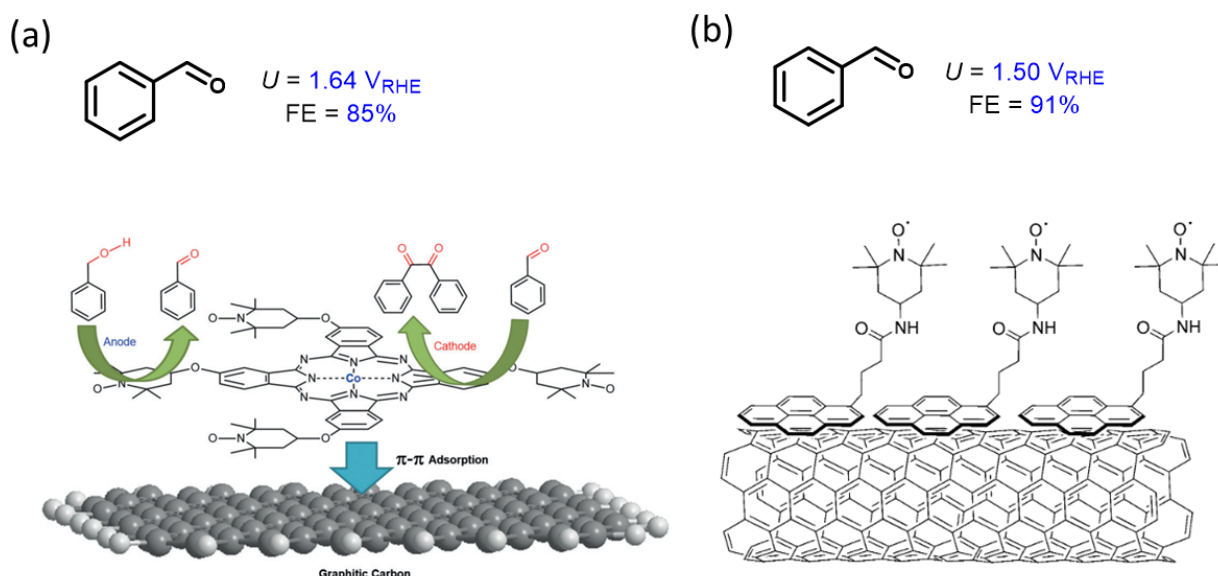
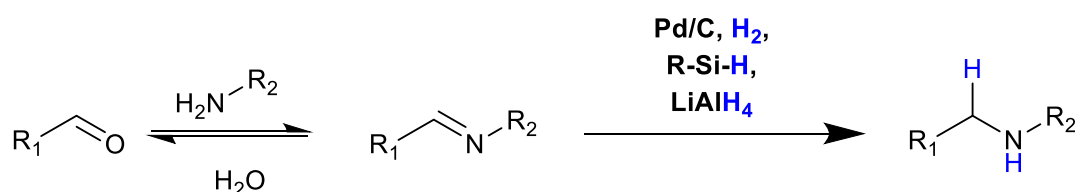


Figure 2.2.8. Non-covalent methods for immobilising TEMPO onto carbon electrodes for benzyl alcohol oxidation using (a) CoPc-TEMPO and (b) pyrene-TEMPO, in pH 10 carbonate buffers. Figures reprinted with permission from publishers.^{152,153}

2.3 Electrochemical Reductive Amination

Amines are very important building blocks in chemistry and are extensively used in polyamides, surfactants and in drugs.^{154,155} Small molecules containing nitrogen moieties are relatively limited in nature usually only appearing in some natural biological small molecules such as amino acids, chitin, and nucleotides; and there is not much more scope to upgrade these compounds further into more valuable chemicals. Due to this, an opportunity presents itself to look at ways of incorporating nitrogen moieties into existing biomass feedstock including furanic compounds, which when aminated provide an even greater library of compounds with more diverse functionalities. Popular industrial methods of incorporating nitrogen into small molecules use toxic hydrogen cyanide, which is produced using the Andrussov process where methane and ammonia are reacted in the presence of a Pt catalyst,¹⁵⁶ which is then used to produce amino acids during the Strecker reaction.¹⁵⁷ Other methods of amine production involve a nucleophilic addition of an amine, followed by a reduction using borohydrides¹⁵⁸ or silanes,¹⁵⁹ to reduce the resulting imines (**Figure 2.3.1**). Electrochemical methods can also be used as a cleaner alternative for this reduction; however, the development of electrochemical C-N bond formation is currently still in its infancy. A recent report by Figueiredo summarised the challenges associated with electrochemical C-N bond formation, stating that mechanisms behind electrochemical C-N bond formation are currently not well understood and require greater attention, as well as the effects of electrode composition, structure, and other reaction parameters.¹⁶⁰

Thermochemical Reductive Amination



Electrochemical Reductive Amination

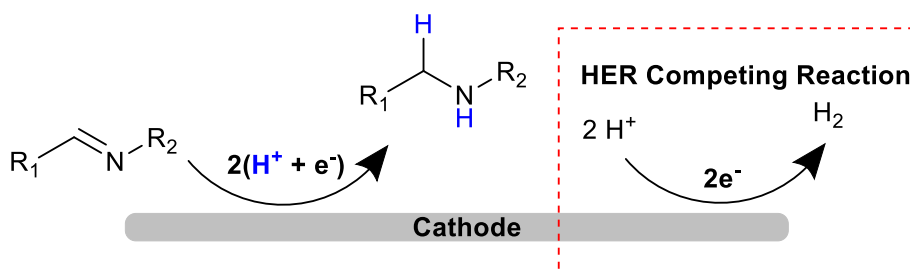


Figure 2.3.1. Comparison of thermochemical and electrochemical reductive aminations.

Once optimised, electrochemical reductive amination can solve the challenges during amine production by eliminating the need for organic solvents and can replace the toxic silane and borohydride reducing agents with non-toxic electrons. A general method has been proposed for an electrochemical reductive amination of carbonyl compounds in **Figure 2.3.1**. This method begins with a nucleophilic addition of an amine to a carbonyl compound to form an imine species which is in equilibrium that can be electrochemically reduced into the amine. An important consideration needs to be considered whereby the imine formation must be pushed to near completion, otherwise, the carbonyl group will be reduced instead into an alcohol, which is now a secondary competing reaction alongside the HER. The first and most popular method of electrochemical reductive aminations was reported by Jeffrey and Meisters¹⁶¹ in 1978 who employed the use of Hg electrodes to produce amino acids using ammonia; nonetheless, in addition to the toxicity of Hg the Faradaic efficiency, at 24%, is rather low. Other methods of electrochemical amine production are reported in the literature however they detail anodic aromatic cross-coupling reactions rather than cathodic hydrogenations.¹⁶² When large aromatic molecules are coupled, organic electrolytes are used because the compounds are not miscible in aqueous electrolyte. It is for this reason; this section will focus on electrochemical reductive amination to produce small nitrogen containing molecules in an aqueous environment.

The obvious source of a clean nitrogen source is ammonia (NH_3). Whilst NH_3 is produced industrially using the Haber-Bosch process, promising work has been done to produce NH_3 electrochemically from nitrogen gas using a lithium-mediated ammonia synthesis.¹⁶³ However, because NH_3 is a very weak nucleophile the equilibrium will need to be shifted by using very high concentrations to produce enough imines. This was demonstrated in works by Fukushima and Yamauchi¹⁶⁴ whereby high concentrations of ammonia (6 M ammonium sulphate buffer) are used to aminate pyruvate on TiO_2 electrodes. Naturally, this may not be reasonable to do on a large scale due to the safety concerns and infrastructure required to use such high concentrations of NH_3 . Instead, the equilibrium reaction may be pushed towards the imine intermediate by using a more powerful nucleophile. In organic chemistry, the strength of a nucleophile can be measured using the Mayr scale,¹⁶⁵ and a list of potential nitrogen-containing nucleophiles measured by their Mayr scale nucleophilicity is denoted in **Figure 2.3.2**.

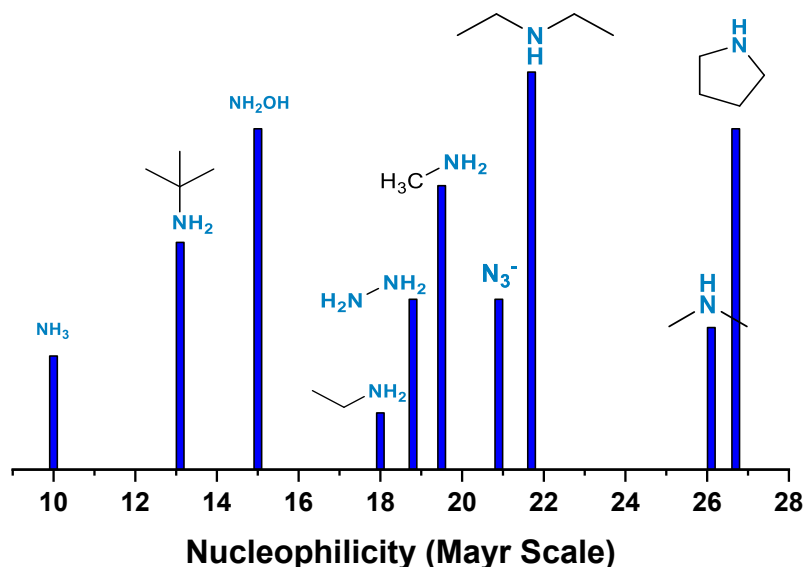


Figure 2.3.2. The nucleophilicity of various primary and secondary amines on the Mayr scale. Figure was produced using values taken from reference.¹⁶⁵

The use of primary amines such as methylamine, and other variants such as hydroxylamine are used as alternative nucleophiles due to an increase in nucleophilicity. Incorporating nitrogen moieties into platform chemicals such as HMF and furfural opens an even larger range of compounds with useful chemical properties. Using primary amines such as methylamine and ethanolamine buffers, Roylance and Choi¹⁶⁶ were able to successfully aminate HMF, DFF and FFCA using electrodeposited Ag electrodes with good selectivity (**Figure 2.3.3**). When primary amines are used, a much lower 0.7 M concentration buffer is required for good amination activity (compared to NH₃), due to the increased nucleophilicity of the primary amine.

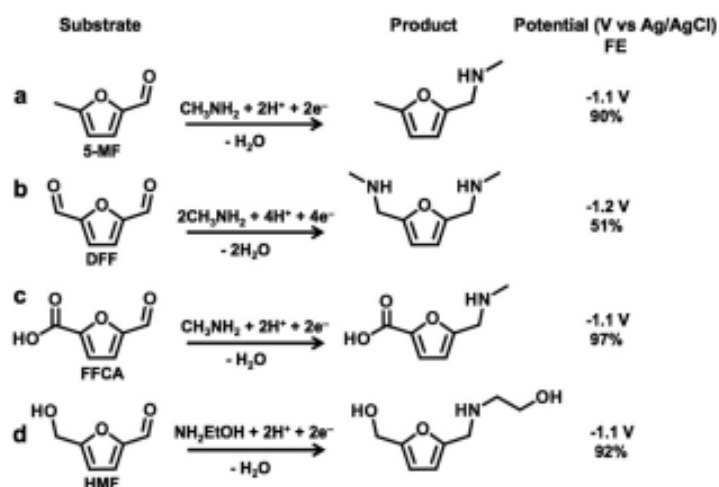


Figure 2.3.3. Products of reductive amination on Ag electrodes of various furanic compounds. Reaction conditions: 0.7 M of chosen amine solution electrolyte (pH ~11).¹⁶⁶

The study also demonstrated that ethanolamine could be added to HMF via reductive amination which produces a compound with greater potential uses due to the added OH functional group (**Figure 2.3.3d**). Electrochemical reductive amination of HMF using ethanolamine was paired with HMF oxidation at the anode using Ti metal-organic frameworks (Ti-MOFs) by Zhang et al.¹⁶⁷ The reductive amination produced a >99% selectivity for the aminated product at -0.60 V vs RHE, with 35% conversion of HMF to FDCA at a 4 mA cm⁻² current density.¹⁶⁷ The study stated that transition metal MOFs are a good alternative to pure metal electrodes for reductive amination due to a greater specific surface area and the presence of specific catalytic sites due to the porous structure of the MOFs. It was suggested that the exposed N-Ti-O active centre was responsible for the efficient reductive amination.¹⁶⁷

Like electroreduction reactions, efficient adsorption of hydrogen as well as biomass compounds are likely required. Transition metal dichalcogenides such as TaS₂ and MoS₂ have been studied for the HER and show good hydrogen adsorption.¹⁶⁸ These materials were tested for their electrochemical reductive amination ability by Zhang et al.¹⁶⁹ during the reductive amination of the furanic compounds furfural, HMF, and 5-MF. TiS₂ nanosheet electrodes showed FEs of up to 38.2% at -0.60 V vs. RHE to produce furfurylamine (**Figure 2.3.4**). It was observed that the FE for the reaction decreases at more cathodic potentials, due to the HER becoming more dominant on the electrode.

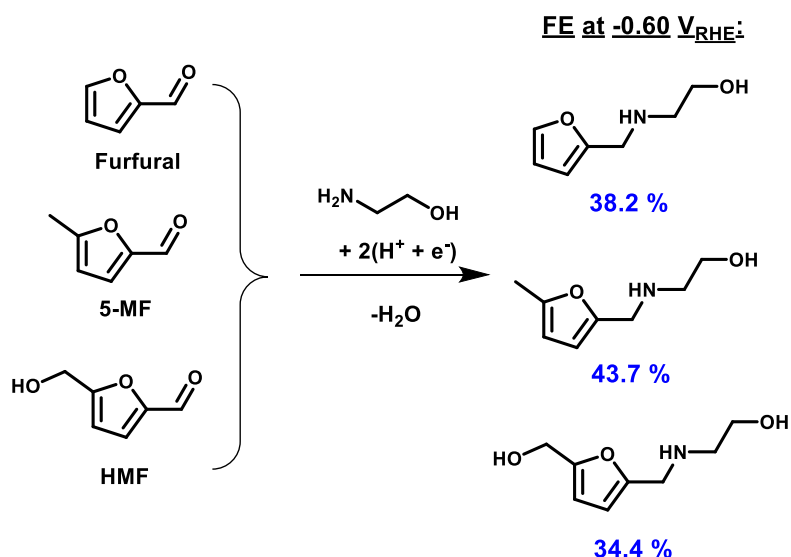


Figure 2.3.4. FEs of aminated products using ethanolamine into furanic compounds on TiS₂. Data points are taken from reference.¹⁶⁹

In another study by Fukushima and Yamauchi, TiO₂ was used to electrochemically aminate different α -ketoacids to produce α -amino acids in 0.1 M HClO₄ (pH 1).¹⁷⁰ Hydroxylamine (NH₂OH) was used as

the preferred nitrogen source which displayed superior nucleophilic activity compared to NH_3 which can be explained by the alpha effect. Only a 1:1 equivalence of NH_2OH to carbonyl bond was required to produce the oxime intermediate, and because of the moderate NH_2OH pK_a (5.94), it was possible to conduct reductive amination reaction in both acidic and alkaline pH. Although a promising method of producing α -amino acids was demonstrated, there was no mention of which optical isomers were produced, which is a significant factor that must be considered if these compounds are used for therapeutic purposes.⁷⁰ This factor is not as important during uses where chirality is not important such as polyamides. A separate study electrochemically synthesised a non-chiral amino acid, glycine, reporting that calcined Ti and TiO_2 displayed the highest efficiency for reductive amination after screening various other metal surfaces.¹⁷¹

The electrochemical reductive amination of straight chain biobased compounds was demonstrated on levulinic acid by Murtz et al.¹⁷² Aminating LA expands the network of potential products available from the biorefinery as LA is a product available from the ring opening of HMF.¹⁷³ The aminated LA can be self-cyclised to produce pyrrolidone species which have uses as surfactants, industrial solvents, and dyes (**Figure 2.3.5a**).¹⁷⁴ Electrodes for the reductive amination were tested including Pb, Cu, Ag, Cd, Zn, Sn and Ni on acetone with methylamine to study selectivity for the reductive amination reaction in a pH 12, 0.5 M KH_2PO_4 electrolyte (**Figure 2.3.5b**). Pb showed good selectivity towards amine formation, but some minor amounts of alcohol were produced due to incomplete nucleophilic addition of the nitrogen source. On Cu and Ag surfaces, the amine was produced more selectively over the alcohol. This result could mean that Cu and Ag bind ketone groups less favourably than Pb electrodes. The low yields on Ni were attributed to the HER occurring at a potential more anodic than that of the reductive amination.

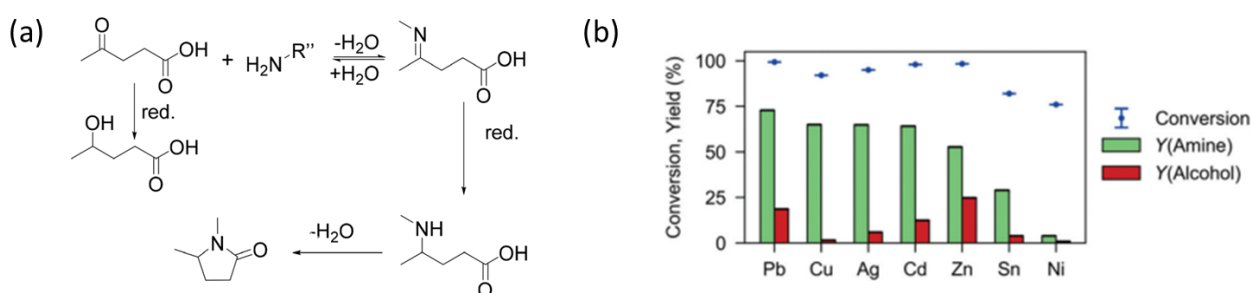


Figure 2.3.5. Electrochemical reductive amination of LA. (a) Scheme of LA amination and cyclisation into pyrrolidones. (b) The yield of amines and unwanted alcohol products produced on metal surfaces. Reaction conditions: 0.5 M KH_2PO_4 electrolyte (pH 12), ketone to methylamine ratio: 1:1.2. Figure reprinted with permission from publisher.¹⁷²

Alongside primary amines, nitrate has also been demonstrated as a possible nitrogen source. Kim et al.¹⁷⁵ proposed a method of electrochemically producing C-N bonds to form glycine from oxalic acid and nitrate on Cu-Hg electrodes, resulting in 43.1% FE with current densities reaching 90 mA cm⁻² in acidic electrolyte. Both oxalic acid and nitrate are good building blocks for this reaction as oxalic acid can be produced from the CO₂RR,⁵⁵ using captured CO₂ emissions, whereas nitrate is an abundant chemical which can be produced through the electrochemical oxidation of nitrogen.¹⁷⁶ It was suggested that the amination mechanism included the partial reduction of oxalic acid to form an aldehyde simultaneous with nitrate reduction to hydroxylamine, followed by a nucleophilic addition and subsequent reduction of the oxime (Figure 2.3.6), with the intermediates of the mechanism seen in the NMR spectra.¹⁷⁵

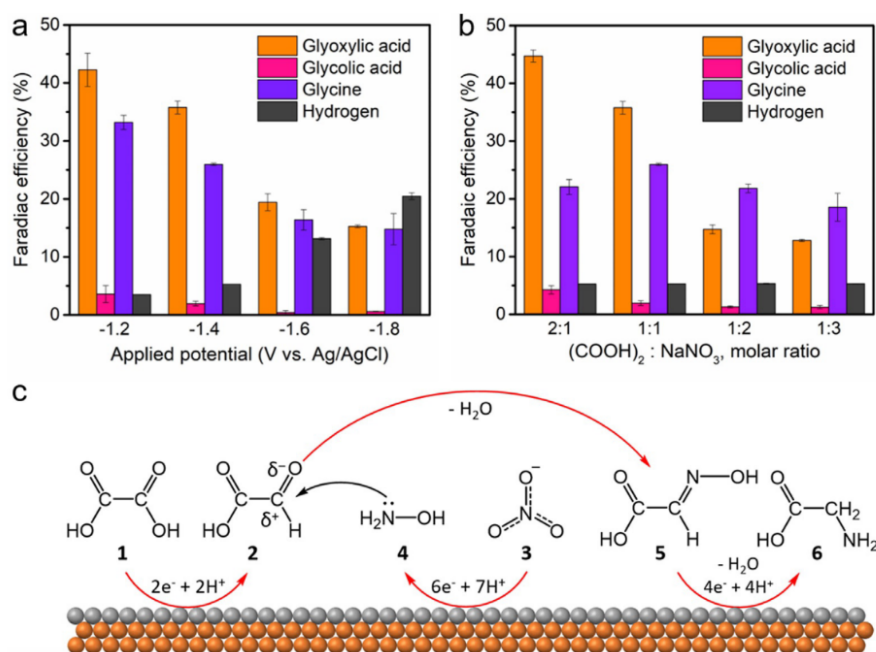


Figure 2.3.6. Electrochemical reductive amination of oxalic acid on Cu-Hg electrodes. FE of products produced at various (a) potentials and (b) different ratios of oxalic acid to sodium nitrate. (c) proposed mechanism for glycine production on Cu-Hg surfaces. Reprinted with permission from reference.¹⁷⁵

Shao et al.¹⁷⁷ attempted to use nitrate amongst other nitrogen sources for the formation of formamide from methanol in 0.5 M NaHCO₃ electrolyte on boron-doped diamond electrodes (BDD), at industrial currents of ~120 mA cm⁻². The mechanism again involves the production of an aldehyde group from methanol, then the addition of a nitrogen source for subsequent reduction into formamide. Interestingly, NH₂OH was not able to produce any formamide at high current densities, explained by the intermediate oxime species being very unstable under these conditions. Here, ammonia was the

only nitrogen source which was able to produce formamide under industrial conditions, and a scale-up 8 L experiment was successfully shown.¹⁷⁷

Electrochemical C-N bond formation was also reported by Rooney et al.¹⁷⁸ using CO₂ to methylate a variety of amines, on cobalt phthalocyanine (CoPc) cathodes. It was determined that CO₂ was reduced to form an HCHO* intermediate, which then was in direct competition between the nucleophilic addition of the amine or direct reduction into CH₃OH. Whilst only low efficiencies were reported, optimisation of this process has great potential for the industrial production of methylamine. A similar experiment was conducted using CO and various amine species on Cu electrodes.¹⁷⁹ It was determined that a ketene intermediate was formed before the addition of the nitrogen source which showed selectivity for the produced amide.

2.4 Electrochemical Ring Opening

Other useful chemicals obtainable from biomass include straight-chain diols, dicarboxylic acids, and diamines. These include compounds such as adipic acid and 1,6-hexadamine which are used to make popular polymers such as nylon.^{180,181} An electrochemical synthesis route to producing straight-chain molecules is possible starting from furanic compounds (**Figure 2.4.1**). Aromatic molecules display better adsorption with metal surfaces compared to straight-chain diols,^{123,130} which can increase electrochemical activity. Derivatives of furanic compounds can undergo ring-opening reactions producing a plethora of useful straight-chain molecules that are otherwise sourced from unsustainable sources. Popular methods of ring opening are done using a thermochemical reduction using PtO_2 and H_2 ,¹⁸² however reductive ring opening reactions are also possible using electrochemistry.

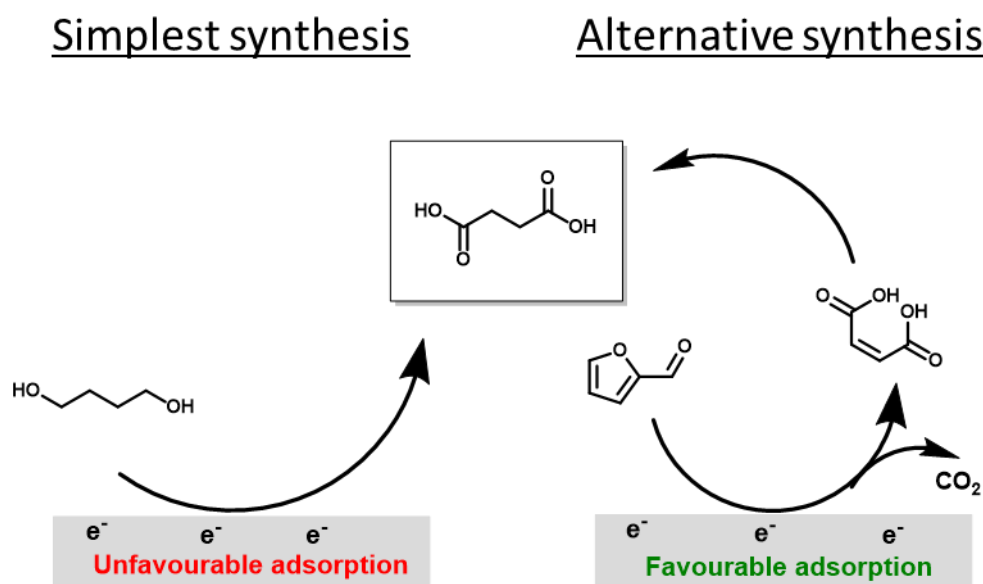


Figure 2.4.1. The general method of electrochemical succinic acid production from aliphatic diols compared to alternative proposed electrochemical synthesis using electrochemical ring opening and subsequent electrochemical reduction.

An example of this was explored by Choi et al.¹⁸³ where maleic acid was produced from furfural, on a PbO_2 anode in a pH 1 acidic electrolyte. It was explained that acidic conditions were necessary to promote ring opening as well as high potentials of 2.0 V vs RHE, which is why PbO_2 was chosen as the anode for its stability and lack of water oxidation activity under these conditions.¹⁸³ Pt and MnO_2 electrodes were also tested, but these electrodes were either too unstable or water oxidation was too dominant to see any maleic acid produced. A small amount of maleic acid was seen in a separate study by Choi et al using Pt during the electrochemical oxidation of HMF in an acidic electrolyte.¹³⁷

Maleic acid was also detected on various metal chalcogenides (CuS, ZnS, PbS, CdS, WS₂, MoS₂, CuO) in a study by Wu et al.¹⁸⁴ during furfural oxidation. The authors stated that on CuS electrodes, 5-Hydroxy-2(5H)-furanone (HFO) was formed as the main product with 77.1% FE before hydroxide radicals promoted ring opening resulting in maleic acid, however, this was unfavourable under these conditions. The electrolyte was a solution of CH₃CN and [Et₃NH]NO₃ in water, which was chosen as the [Et₃NH]NO₃ was able to speed up the formation of hydroxide radicals from water, promoting the production of HFO and maleic acid (**Figure 2.4.2**). CuS was the best performing catalyst which is advantageous,¹⁸⁵ compared to PbO₂ and Pt in terms of price.

The rate of formation of HFO was stated as the limiting factor of maleic acid production during a study by Roman et al.¹⁸⁶ whilst exploring the electrochemical oxidation of furfural on Au/C electrodes. Furoic acid was seen as the main oxidation product at low potentials (0.80 V vs RHE), whereas it was found that relatively high potentials (>1.20 V vs RHE) and acidic electrolyte (0.25 M HClO₄) were needed to produce HFO of any significant amount, which also yielded very small amounts of maleic acid. An important piece of information to consider was the reported inhibition of furfural oxidation due to furoate formation, which poisons the Au surface. This could explain why high potentials are needed to force maleic acid production, as it could help with greater rates of furoate desorption. A comparison of all suggested mechanisms is denoted in **Figure 2.4.2**.

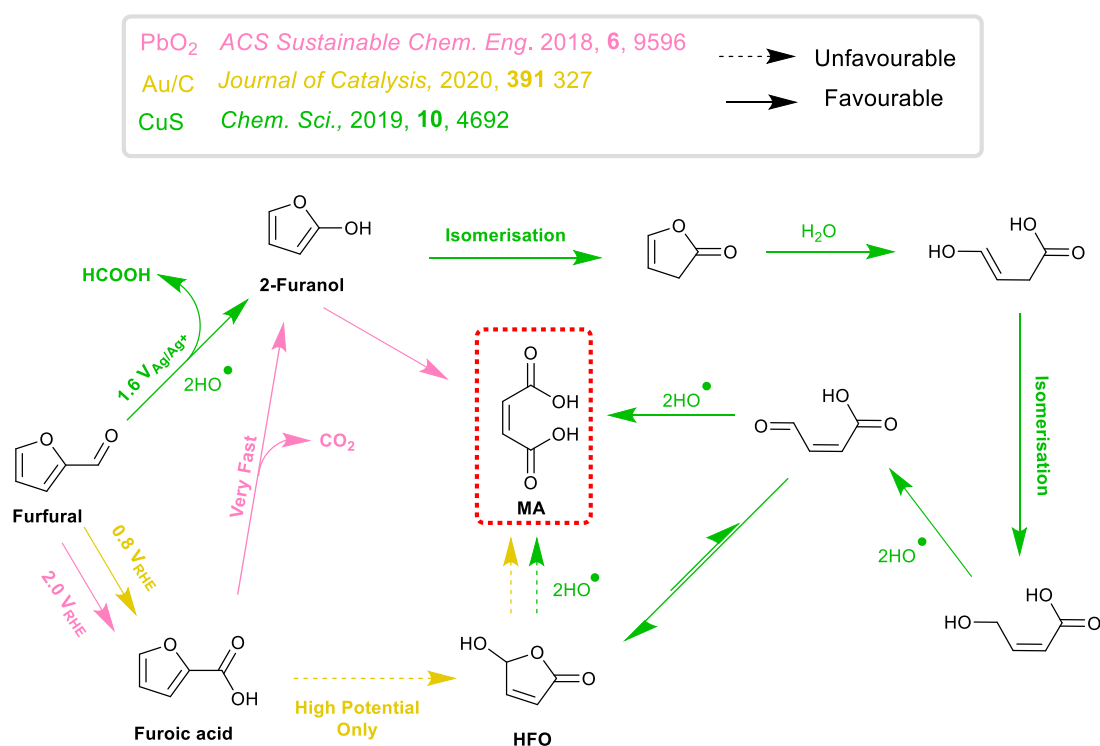


Figure 2.4.2. Proposed mechanisms for the electrochemical formation of maleic acid (MA) using PbO₂, Au/C, and CuS anodes. Mechanisms taken from references.^{183,185,186}

Cathodic potentials may also be used for electrochemical ring opening reactions. This method of ring opening provides greater benefits than those of anodic ring-openings because less toxic materials are stable at these potentials. Roylance first demonstrated it was possible to reduce HMF into 2,5-hexanedione using a Zn electrode in acidic electrolyte (pH 2 sulphate buffer) at -0.89 V vs RHE, with up to 72.4% FE.¹⁸⁷ 2,5-hexanedione can subsequently be converted into useful chemicals such as *n*-hexane and *p*-xylene – a precursor to terephthalic acid.¹⁸⁸ A proposed mechanism of this conversion was also provided (**Figure 2.4.3**) which suggested a Clemmensen-type reduction first occurred to remove the aldehyde group from HMF, followed by ring opening.

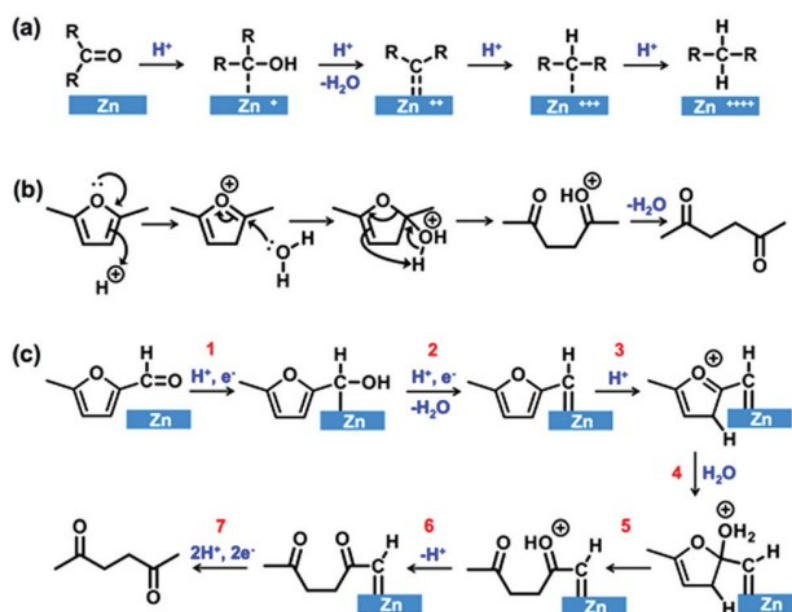


Figure 2.4.3. Proposed mechanisms for carbonyl bond reduction in a pH 2 sulphate buffer. (a) Clemmensen reduction on Zn under acidic conditions. (b) acid catalysed ring opening of DMeF, (c) Electrochemical ring opening of furfural on Zn electrodes. Figure was reprinted with permission from publisher.¹⁸⁷

The research on aqueous electrochemical reductive ring opening is very limited in the available literature, and other papers regarding ring opening reactions were conducted in organic solvents. Zn reduction may already provide a cheap and effective method of opening furan ring systems, and no publications on ring opening reactions in basic conditions were found.

2.5 The Missing Pieces

As discussed in this chapter, the electrification of chemical synthesis is an effective way of revolutionising the way clean fuels and chemicals are sourced. It is appreciated in literature that the products obtained from the upgrading of furanic platform chemicals are viable for replacing chemicals sourced from petrochemical feedstock, however, more work is needed to address some issues that are stopping this becoming feasible. **Figure 2.5.1** links some of the electrochemical reactions that were discussed in this chapter, highlighting remaining issues that need to be solved. One of the biggest challenges in electrosynthesis is product selectivity, for which developing new catalysts and optimising reaction parameters can help solve. Whilst most reactions were reported in a non-continuous process, there is no reason to assume a continuous process in an MEA configuration is not possible. The continuous electrochemical production of furanic compounds is still in its infancy and has not been detailed much in the literature, which opens opportunities to study this topic. As there is little for baseline aims for this process, inspiration from commercial water electrolyzers can set a few initial aims. These electrolyzers operate at around $100\text{--}500\text{ mA cm}^{-2}$ of current density,¹⁸⁹ and so new biomass electrolyzers will include an essential initial minimum current density of between $50\text{--}100\text{ mA cm}^{-2}$, to be eventually increased to $>500\text{ mA cm}^{-2}$. The initial biomass feedstock needs to be controlled but eventually a target of up to 0.5 M should be made relevant.

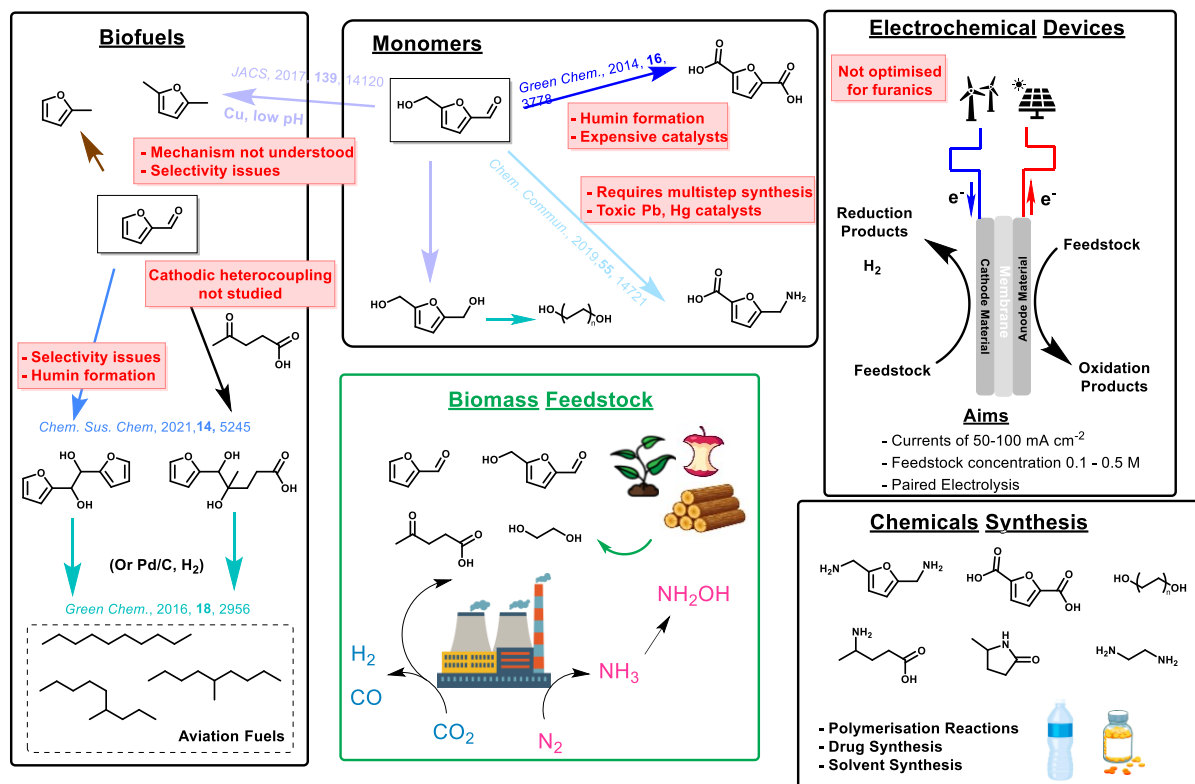


Figure 2.5.1. Combined electrochemical conversion of biomass compounds. Limitations to be addressed are highlighted in red boxes. Conversions are taken from references.^{108,126,143,164,187}

In addition to the gaps in experimental literature, other conclusions are made which direct starting points for further experimental work. These include:

- **Binding properties between the electrode and biomass plays a major role in determining selectivity.** The choice of electrode material for furfural and HMF reductions was seen as arguably the biggest factor in product selectivity and Faradaic efficiency, especially during furfural reduction reactions. Cu electrodes were the only reported monometallic material that produced 2-MF in good amounts, however the mechanisms on this surface are not well understood. Chapter 4 will attempt to unravel the mechanisms surrounding 2-MF production on Cu. It was also determined that hydrofuroin holds great promise as a sustainable precursor to drop-in jet fuels, however its production using current electrochemical means is quite challenging due to poor activity, plus the selectivity issues associated with radical coupling. Chapter 4 attempts to tackle this problem by synthesising new catalysts guided by theoretical calculations based on binding energies between said catalysts and furfural.
- **Non-electrochemical steps during electrosynthesis are important.** We have learnt that electrosynthesis is not just confined to the reaction happening on the electrode surface, but non electrochemical steps such as OH deprotonation on alcohols,¹³² or a nucleophilic addition of a nitrogen source onto a carbonyl bond are important too, and need to be optimised. Secondly, methods to extract electrochemically produced products must be efficient, preferably using as few reagents as possible. This is especially important during multistep electrosynthesis processes whereby reagent heavy separation techniques should be minimised. Methods to address these issues will be explored in Chapter 5.
- **Industrially relevant electrosynthesis using HMF and furfural needs improving.** More focus is needed on the scale-up from laboratory experiments to an industrial synthesis. This will require robust electrode materials which are inexpensive, highly selective, and can work at industrial currents for long periods. Chapter 6 will attempt to develop new catalysts for HMF oxidation to produce FDCA in a continuous process, to try and bring commercialisation of this process one step closer.

3 | Experimental Methods

3.1 Materials

All materials used in this thesis were used as received. Furfural (99%, Sigma Aldrich), FAL (98%, Sigma Aldrich), HMF (99%, Sigma Aldrich), FFCA (99%, ThermoFisher), DFF (97%, Sigma Aldrich), HMFA (95%, Sigma Aldrich), furfurylamine (99%, Sigma Aldrich), HMFA (97%, FluoroChem), DMSO (analytical standard, Sigma Aldrich), NafionTM Ionomer (5% in ethanol, Sigma Aldrich), NafionTM 117 membranes (Fuel Cell Stores), copper phthalocyanine (CuPc, 99% Sigma Aldrich), cobalt phthalocyanine (CoPc, 97% Sigma Aldrich), multi-walled carbon nanotubes (MWCNT, 95% Nanocyl), KOH (Ultrapure, Merck), HClO₄ (Ultrapure, Merck), Ag foil (99.97%, GoodFellow), Pb foil (99.99%, GoodFellow), Au foil (99.9%, GoodFellow), Sn foil (99.95%, Goodfellow), carbon paper (Freudenberg H14, Fuel Cell Stores), dimethylformamide (DMF, 99.9% Sigma Aldrich), 4-amino TEMPO (97%, Sigma Aldrich), EDC (commercial grade, Sigma Aldrich), Sulfo-NHS (98%, Sigma Aldrich), 2-morpholinoethanesulfonic acid (MES) buffer (99% saline, Thermo Fisher), potassium phosphate dibasic (98%, Sigma Aldrich), potassium phosphate monobasic (99%, Sigma Aldrich), potassium perchlorate (98%, Sigma Aldrich), lithium perchlorate (99.9%, Sigma Aldrich), IrO_x powder (99%, Alfa Aesar), Ag₂SO₄ (98%, Sigma).

3.2 Electrochemical Experiments

All electrochemical experiments were conducted using an Ivium Vertex One potentiostat at room temperature. For experiments done in a H-Cell, a Hg/HgSO₄ reference electrode (SI Analytics) was used which was calibrated against a RHE, hence, all potentials reported in this thesis are on the RHE scale. Pure metal electrodes were prepared by using fine sandpaper on the surface, then were ultrasonicated in ethanol for 15 min before use. After washing with MilliQ water (18.2 MΩ·cm) the foils were held at -0.75 V vs RHE for 10 min, to try best reduce any surface oxides. Some voltage loss occurs due to the resistance of the electrolyte solution between the reference and working electrode known as the *iR* drop. All electrochemical measurements were *iR* corrected using electrochemical impedance spectroscopy (EIS) – a technique used measure the resistive and capacitive properties of an electrochemical interface. EIS was used to obtain values of uncompensated resistance, which were then used in correcting the *iR* drop. The values of the uncompensated resistance remained relatively constant between experiments, with 5-10 Ω for carbon felt and metal foil electrodes, and between 50-60 Ω for a glassy carbon electrode. 41 frequencies were used starting at 10,000 Hz ending at 1 Hz, with an amplitude of 0.03 V. An example EIS plot for a typical 1 x 1 cm² carbon paper electrode is shown in **Figure 3.2.1**.

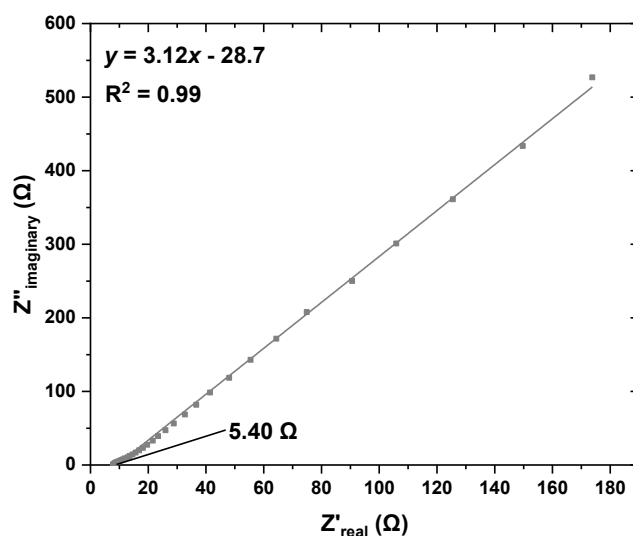


Figure 3.2.1. EIS of $1 \times 1 \text{ cm}^2$ carbon paper electrode in a 0.1 M potassium bicarbonate-carbonate buffer (pH 10).

H-Cell Setup

Electrochemical experiments were carried out in a three-electrode, three-compartment custom made H-Cell (Cambridge Glassware, **Figure 3.2.2**). The anolyte and catholyte chambers were separated with a Nafion™ 117 membrane, with argon gas (99.99%, BOC) bubbled into the electrolyte for 10 min before electrochemistry to purge any dissolved oxygen. No argon gas was bubbled during electrochemical measurements thereafter. Nafion™ membranes were activated before use by heating for 30 mins each in 0.5 M H_2SO_4 , MilliQ water, and 0.1 M potassium bicarbonate buffer.

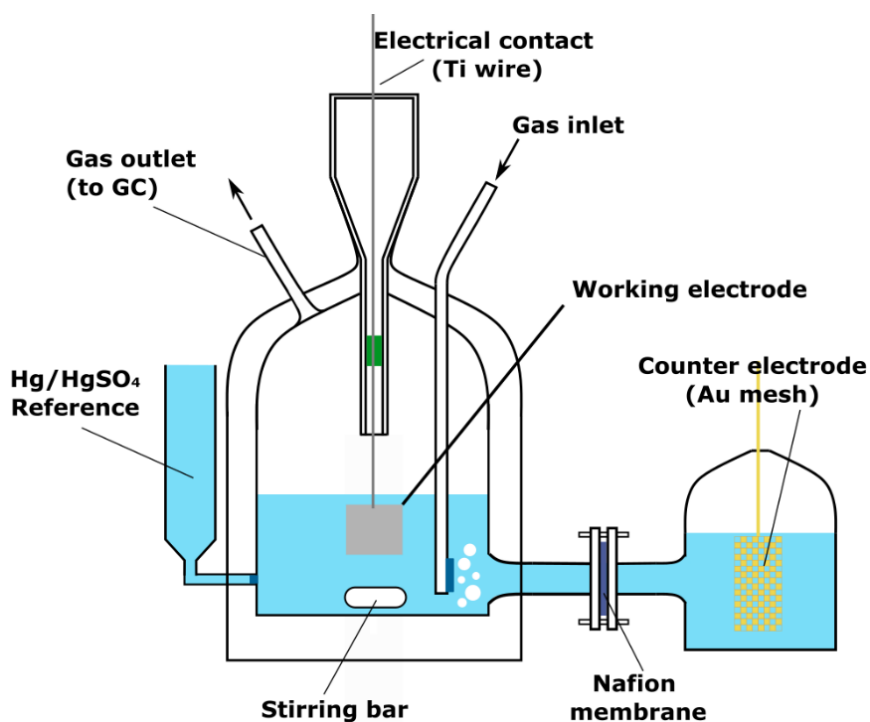


Figure 3.2.2. Electrochemical H-Cell setup used in this study. GC – gas chromatography.

MEA Setup

The zero-gap MEA cell was designed and built at Imperial College London (**Figure 3.2.3**), using polyetheretherketone (PEEK). The cell design was based on a cell previously used for the CO₂RR,¹⁹⁰ with the only difference being replacing the serpentine flow-field with a 1 x 1 cm² square with 1 mm depth for both plates. Silicon gaskets were added between layers to keep the cell watertight with a Nafion™ membrane sandwiched between. Electrochemical experiments using the MEA setup used a two-electrode setup using a Pt mesh or IrO_x nanoparticles as cathode and anode counter electrodes respectively. The working electrode was spray coated onto carbon paper and was separated from the counter electrode by a Nafion™ membrane. Al foil was used as the electrical connection. The flow of electrolyte was controlled using a peristaltic pump (JIHPUMP) and was set at a flow rate of 11 mL min⁻¹.

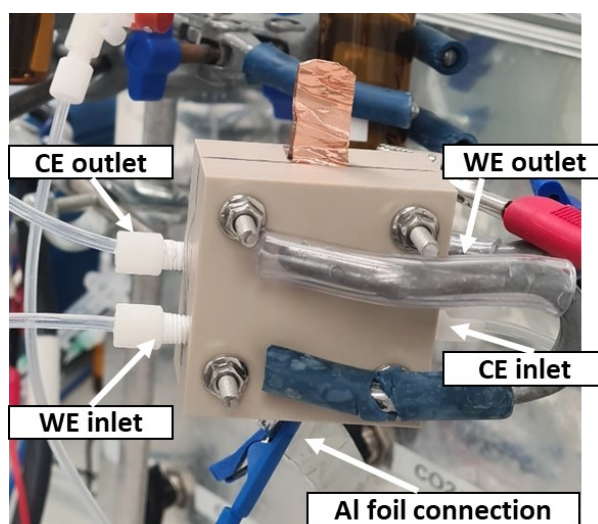


Figure 3.2.3. MEA configuration used for continuous electrochemical synthesis. CE – counter electrode, WE – working electrode.

Cyclic Voltammetry and Linear Sweep Voltammetry

CV is an electrochemical technique that is used to study oxidation and reduction properties of an electrode material. It involves scanning the working electrode linearly over a range of potentials whilst recording the current flowing between the reference and working electrode as a function of the potential. LSV is a similar technique to CV but does not sweep the potential backwards to reach the starting potential. The scan rate for all electrochemical experiments was 50 mV s⁻¹ unless stated otherwise.

Chronoamperometry

Chronoamperometry is an electrochemical technique that measures the current flowing between the working and reference electrode as a function of time, at a set potential. In this work, the potential is set to a value that will cause a biomass chemical to be oxidised or reduced into a different chemical. Theoretical charges based on current densities were estimated using the Faraday equation (**equation 3.1**) where n , I , t , F , and z are moles, current density, time, Faraday constant, and electrons transferred per mole respectively.

$$n = \frac{It}{Fz} \quad \text{Eqn. 3.1}$$

3.3 Analytical Techniques

3.3.1 HPLC.

HPLC is an analytical technique which can separate compounds in a mixture and can be used to quantify each compound.¹⁹¹ A liquid sample is injected into a column using a mobile phase to separate the compounds that constitute the sample. These are then detected using a UV-Vis detector in the machine.

All HPLC measurements were conducted using an Agilent 1260 Infinity II HPLC machine equipped with a UV-Vis detector. For furfural reduction experiments, 0.5 mL aliquots were taken and diluted twice using CH₃CN. The aliquots were fed through a Zorbax SB C-18 column (4.6 x 50mm, 3.5-micron, Agilent Technologies), with a fixed flow rate of 1 mL min⁻¹ using a mobile phase of water: CH₃CN (88.7: 11.3 ratio). The column temperature was maintained at 35 °C and the UV-Vis detector was set at 220 nm. Furfural and FAL had retention times of 1.62 and 1.35 mins respectively, whereas hydrofuroin produced two peaks at 1.90 and 4.20 min, accounting for the two isomers produced.

For HMF oxidation experiments, liquid aliquots were passed through an Aminex HPX-87H column (300 mm x 7.8 mm, BioRad), using a mobile phase of 5 mM H₂SO₄ whilst the column was maintained at 65 °C, with the UV-Vis detector set at 254 nm. FDCA, FFCA, HMFA, HMF, and DFF eluted at retention times of 15, 19, 21, 28, and 33 mins respectively.

Quantification of the possible products were done by passing solutions of known concentrations through the respective columns and producing a calibration curve of the integrated area as a function of concentration. The calibration curves used in this thesis are depicted in **Figure 3.3.1.1**.

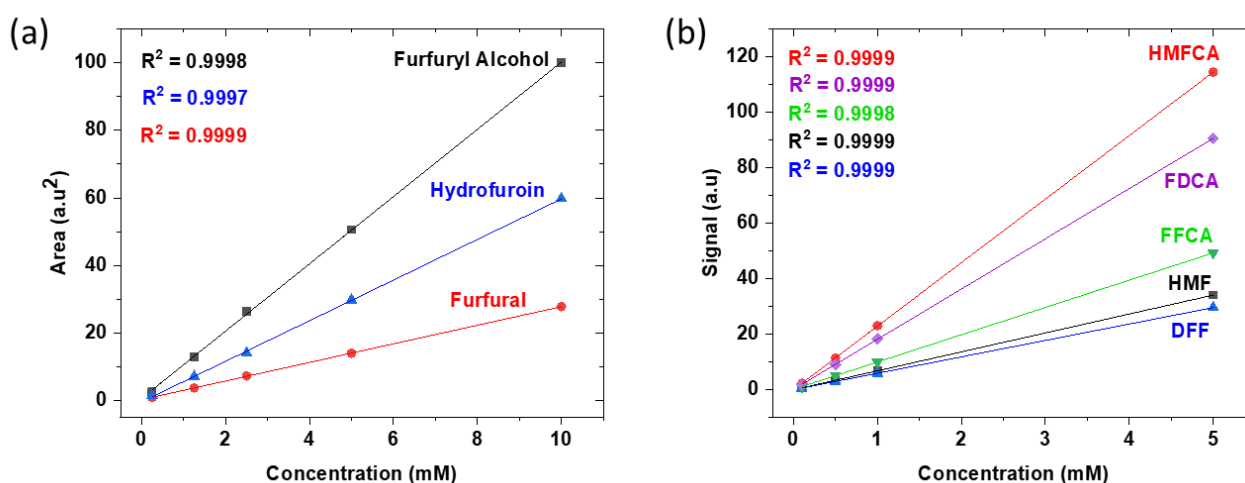


Figure 3.3.1.1. HPLC calibration curves used for (a) furfural reduction experiments and (b) HMF oxidation experiments.

3.3.2 Gas chromatography.

Gas chromatography (GC) is an analytical technique which can separate gaseous elements/compounds that can be vapourised without degrading.¹⁹² The vaporised sample is fed through a column using a carrier gas and which results in the separation of compounds with different retention times.

GC was performed on an SRI Instruments MG#5 machine and was purely used to quantify hydrogen gas. After a stable chronoamperometry was reached (usually after 5 min), the effluent was injected into the GC using argon as the carrier gas. The machine was equipped with a thermal conductivity detector which displayed the signal of H₂ gas.

3.3.3 NMR spectroscopy.

NMR spectroscopy is an analytical technique that uses the magnetic properties of atomic nuclei to obtain information about the structure and chemical environment of a molecule.¹⁹³ The application of a strong magnetic field to a sample aligns nuclei with this field, then radiofrequency radiation is applied to excite these nuclei. The amount of radio waves that are absorbed is dependent on the chemical environment around the nucleus because the magnetic field is influenced by the electron density around it.

NMR was performed on a Bruker 400 MHz spectrometer with quantification of compounds done by adding known concentration of dimethylsulfoxide (DMSO) as an internal standard. The concentration of the analyte was calculated using **equation 3.2** where C_x , I_x , I_s , P_x , P_s , C_s represent analyte concentration, analyte integral, internal standard integral, number of analyte protons, internal standard protons, and internal standard concentration, respectively. ¹H nuclear Overhauser effect spectroscopy (NOESY) was used to suppress the water peak signal to identify peaks which would otherwise be covered at around 4-5 ppm.

$$C_x = \frac{I_x}{I_s} \times \frac{P_s}{P_x} \times C_s \quad \text{Eqn. 3.2}$$

3.3.4 Scanning electron microscopy

SEM is a type of microscopy used to image the surface of a sample. It essentially works by scanning a beam of electrons across a surface that interact with atoms on the surface, producing various signals that are picked up by detectors.¹⁹⁴

For SEM images, a Zeiss Auriga machine was used with the acceleration voltage of 5 kV, aperture size of 30 μm , and working distance of 5 mm. Energy-dispersive X-ray spectroscopy (EDX) analysis was also performed on the same SEM machine with the acceleration voltage of 20 kV, aperture size of 60 μm , and working distance of 10 mm.

3.3.5 HAADF-STEM

HAADF-STEM is a microscopy technique that uses a detector to collect electrons that have been scattered at high angles. These electrons are scattered by the atomic nuclei and the intensity of the scattering is proportional to the atomic number. This makes HAADF-STEM ideal for elemental mapping as the images are sensitive to variations in atomic number.¹⁹⁵

HAADF-STEM was used to image single atoms and was carried out on an JEOL ARM200F microscope at 200 kV with the images analysed using Gatan software. Samples were deposited onto an Ag grid under dry conditions to avoid contamination.

3.3.6 UV-Vis absorption spectroscopy

UV-Vis is a spectroscopic technique that can be used to study the optical properties of a sample.¹⁹⁶ A dissolved sample is placed in a cuvette and a beam of light is passed through. The light then passes through a grating resulting in it dispersing into its component wavelengths, and the amount of light absorbed by the sample at each wavelength is measured by a detector.

Solution UV-Vis spectroscopy was performed on a UV-1601 Shimadzu UV-Vis spectrometer. Samples were dissolved and measured in chloroform (0.1 mg mL^{-1}).

3.3.7 Operando optical spectroscopy

It is possible to couple electrochemical experiments with UV-Vis spectroscopy.¹⁹⁷ In such experiments, a light beam is passed through a catalyst-loaded electrode instead of a cuvette and can be used to monitor changes in oxidation states and concentration of a catalyst on an electrode surface (**Figure 3.3.7.1**).

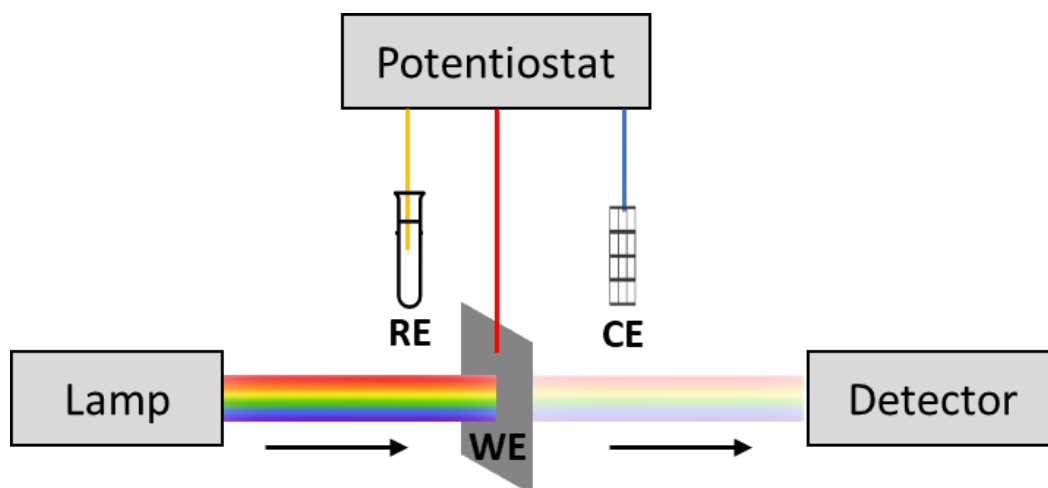


Figure 3.3.7.1. Diagram of the *operando* optical spectroscopy setup. RE, WE, and CE stands for reference, working, and counter electrode respectively.

Reflectance mode *operando* optical spectroscopy measurements were done by first spray-coating NDI-4-TEMPO onto a 1 x 2 cm² carbon paper. A custom made three-electrode cell was produced, and a stabilised 10 mW tungsten-halogen light source was used (Thorlabs SLS201L) which had a collimating add on (SLS201C). The light which was reflected by the sample was collected using a liquid light guide (1 cm, Edmund optics). The detector was kept at -80 °C throughout the experiment to maintain a high signal-to-noise ratio. For the electrochemical measurements, the scan rate was 5 mV s⁻¹ and the equilibrium time at each potential was 10 seconds followed by a measurement of the optical spectra.

3.3.8 XPS

XPS is a surface-sensitive spectroscopic technique used to analyse the surface composition for a sample.¹⁹⁸ XPS works by irradiating a sample with x-rays which results in electrons from the sample being ejected, and the energy of these electrons is measured. The binding energy of electrons are influenced by their chemical environments, and the relative intensity of the collected electrons can be used to determine the percentage composition of a sample.

XPS measurements were taken using a Thermo Fisher K-alpha high throughput system, using a 180° double focusing hemispherical analyser with an area detector. 400 µm x-ray spot size using an Al-K α source. Nominal analysis chamber pressure was set to 2 x 10⁻⁸ mbar before the start of the experiment. Peak fitting and analysis were done using Avantage software.

3.3.9 Electrochemistry-mass spectrometry (EC-MS)

Electrochemistry-mass spectrometry is an analytical technique that can measure gases and volatile species in real-time.¹⁹⁹ About 100 μm depth of aqueous electrolyte is sandwiched between the working electrode and a hydrophobic chip (Figure 3.3.9.1a). The pores of the hydrophobic chip allow volatile compounds to travel through to the mass spectrometer, but do not allow water to travel through.

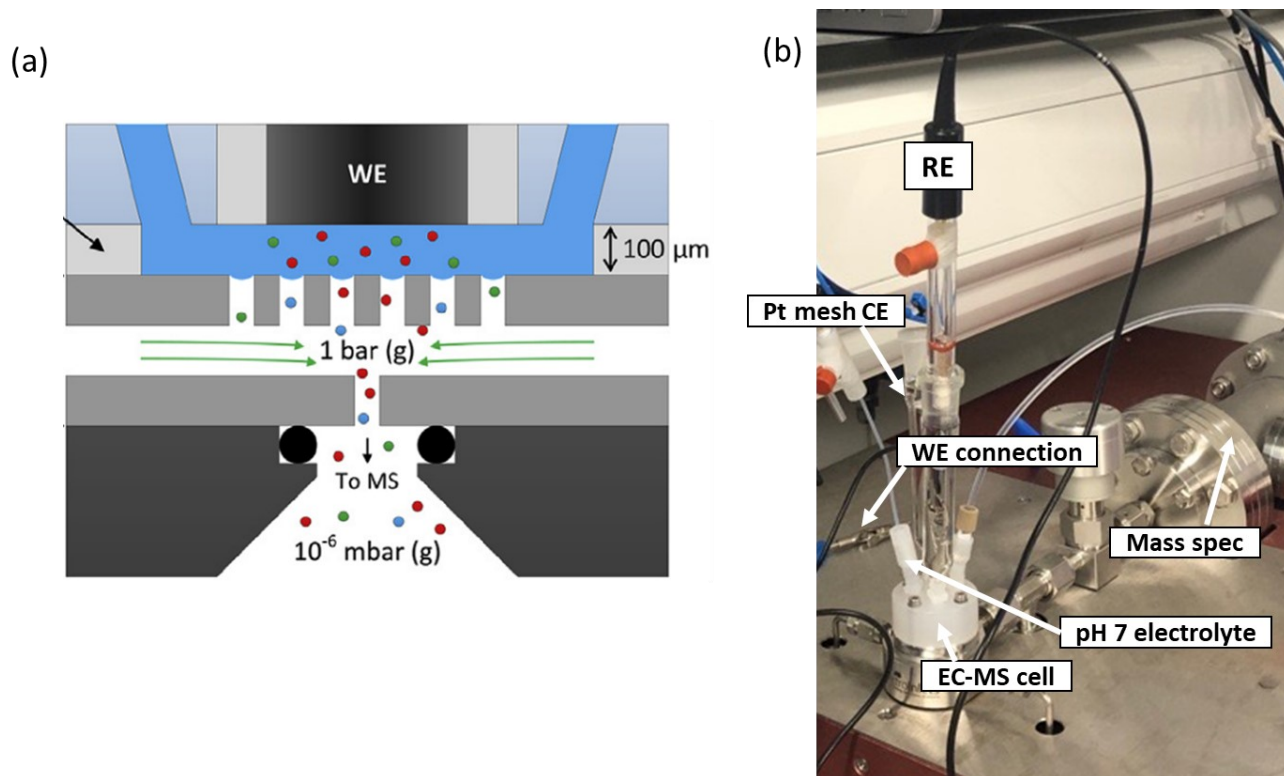


Figure 3.3.9.1. (a) illustration of EC-MS setup used in this thesis. (b) Setup of EC-MS cell. CE – counter electrode, WE – working electrode, RE – reference electrode. Electrolyte used was 0.1 M potassium phosphate buffer (pH 7). Illustration (a) was reprinted with permission from the publisher.

Organic catalyst stability tests were performed on chip-based electrochemistry mass spectrometry (EC-MS) (Spectro Inlets). 1 mg of an organic catalyst and 15 μL of NafionTM ionomer were dispersed into acetone, then drop-casted onto a 5 mm diameter glassy carbon disk (PINE Research), which was used as the working electrode to achieve a final loading of 0.08 mg cm^{-2} . A home-made reversible hydrogen electrode (RHE), and Pt mesh were used as reference electrode and counter electrode, respectively. To avoid CO_2 production from the electrolyte, a 0.1 M pH 7 phosphate buffer was used as the electrolyte. Before each stability measurement, a linear sweep voltammetry (LSV) from 0 V to -0.8 V vs. RHE with the scan rate of 50 mV s^{-1} was conducted to activate the catalyst. Subsequently,

constant potentials of 1.4 V, 1.5 V, 1.6 V, 1.7 V, and 1.8 V vs. RHE were successively applied to the catalyst for 90 s each, using chronoamperometry technique. Mass signals of 2, 32, and 44 were monitored *in situ* to detect the amount of H₂, O₂, and CO₂ generated. Between each of the chronoamperometries, the working electrode was relaxed at open circuit potential (OCP) for 30 min for all mass spectrometry signals stabilised to their background. Electrochemistry and mass spectrometry datasets were combined and analysed using Ixdat Python package (<https://github.com/ixdat/ixdat>).

3.3.10 Time-of-flight secondary ion mass spectrometry (ToF-SIMS)

ToF-SIMS is a surface analysis technique with a depth analysis of a few nanometers. A focused beam of primary ions sputters atoms and molecules from a sample surface. The secondary ions are then accelerated into a ToF mass spectrometer.²⁰⁰

ToF-SIMS (ION-TOF V GmbH) was done using a Bi₃⁺ primary ion gun at 25 keV and 0.5 pA beam current, with a 5 µm spot size on a 100 x 100 µm field of view, and 256 x 256 pixels rastered in sawtooth mode for 25 min (100 µs cycle time). For samples that were tested post-chronoamperometry, no ionomer was used during the electrochemistry to avoid fragments counts from the ionomer.

3.4 Synthesis

3.4.1 Sputter deposition

Sputter deposition is a physical vapour deposition technique used to deposit atoms from a target onto a substrate from a plasma. In this context, sputter deposition was used to create films of manganese oxide and platinum onto carbon paper for use as electrodes.²⁰¹ Sputter deposition was carried out using an AJA Magnetron sputter deposition tool, using Pt, Ti, and Mn targets (99.9%, AJA). For sputter deposition onto carbon paper, a 30 nm layer of Ti was first deposited to help following sputtered material to better adhere to the surface.

Pt: For a 200 nm Pt layer, the conditions used were a 30 W power source at 3 mTorr, with argon gas flowing at a rate of 20 mL min⁻¹, for 15 min.

MnO_x: for a 200 nm MnO_x layer, a 200 W power source was used at 3 mTorr, with Ar and O₂ gas flowing at 20- and 5- mL min⁻¹ respectively, for 45 min.

3.4.2 Synthesis of CoPc and CuPc Catalysts

CuPc and CoPc were physisorbed onto MWCNT sidewalls using the procedure reported by Zhang et al.⁶⁷ A 1:20 Cu/CoPc to MWCNT ratio was added to 20 mL of DMF and left to sonicate in an ice bath for 1 h then was stirred at room temperature for 20 h. The suspension was filtered under vacuum and then washed with copious amounts of DMF, ethanol, and MilliQ water in order then left to dry overnight at 80 °C. The final wt/wt% metal loadings were between 1.21 – 1.65 % and were confirmed using XPS (**Figure 4.6.1c**), and HAADF-STEM images were taken to observe the presence of individual single-atoms of copper (**Figure 4.6.1b**).

3.4.3 Synthesis of Hydrofuroin Standards

Hydrofuroin was quantified using HPLC, however hydrofuroin standards were not available to be purchased from vendors. Instead, hydrofuroin was synthesised using the Mg-mediated pinacol coupling of furfural following the procedure of Zhang et al.,²⁰² and both isomers are combined for simplicity. Furfural (200 mg, 1.89 mmol) and Mg turnings (1 g, 41 mmol) were stirred together in 0.1 M NH₄Cl at room temperature for 24 h. The reaction mixture was then quenched using 3 M HCl and then extracted three times with 10 EtOAc, with the combined organic phases further extracted with saturated NaCl and NaHCO₃. The crude product was achieved after the EtOAc was evaporated under reduced pressure, and the crude product was purified on silica via column chromatography using a gradient of n-hexane and EtOAc. The pure product was a brown oil (38 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.29 - 7.25 (m, 2H), 6.24 - 6.14 (m, 4H), 4.94 - 4.90 (s, 2H). (**Figure A1**)

3.4.4 Electrodeposition of Ag Foam Electrodes

The electrodeposition of Ag foam was done using the method of Wang et al.²⁰³ Ag₂SO₄ is insoluble in water, so a complex ion using thiocyanate ligands was used to make a water-soluble Ag compound. A solution was prepared which contained Ag₂SO₄ (0.01 M), KSCN (1.5 M), NH₄Cl (0.5 M) and sodium citrate (0.01 M) in MilliQ water, leaving the solution to stir for 30 min at room temperature until no solids remained in solution. A -4.0 V potential was applied to the solution using a two-electrode setup, with Ti mesh as the cathode and Ag mesh as the anode respectively, for 120 s to complete the deposition. SEM images were taken to confirm successful electrodeposition (**Figure 5.8.1b**).

3.4.5 Synthesis of TEMPO-MWCNTs

TEMPO-MWCNTs were synthesised using carboxyl functionalised MWCNTs and 4-amino TEMPO using amide EDC/sulfo-NHS mediated amide coupling. MWCNTs were functionalised by refluxing in a 3:1 mixture of H₂SO₄ (96%) and HNO₃ (70%) respectively, for one hour. The final concentration of the acid-MWCNT mixture was 5 mg mL⁻¹. The mixture was neutralised using 3 M KOH and the carboxyl functionalised MWCNTs were filtered under vacuum and washed with MilliQ water then left to dry at 80 °C overnight.

For the amide coupling reaction, 5 mg of the carboxyl functionalised MWCNTs was added to 10 mL of MES buffer containing 4 mg of EDC and left to stir for 10 min at room temperature. 11 mg of sulfo-NHS was then added and the mixture was left to stir at room temperature for a further 30 min. Lastly, 4-amino TEMPO (10 mg) was added to the solution after raising the pH to 7 using a phosphate buffer, and was stirred at room temperature overnight. The solid TEMPO-MWCNTs were filtered under vacuum and washed with MilliQ water then left to dry overnight at 80 °C.

3.4.6 Catalyst Ink Preparation

For the single-atom catalysts, the catalysts was added directly to a MilliQ water to isopropanol mixture (85:15) with NafionTM ionomer (1:0.5 catalyst to NafionTM wt/wt ratio) to achieve a final catalyst concentration of 1 mg mL⁻¹. The ink was sonicated for 30 min in an ice bath and then drop casted accordingly onto carbon paper electrodes. For TEMPO experiments, the NDI-TEMPO catalysts were added to a relevant carbon support (**Table 3.8.1**) in acetone, with NafionTM ionomer added to some experiments, then sonicated in an ice bath for 30 mins. The ink was then either drop-casted or spray coated onto a carbon paper electrode.

Carbon material	Surface area (m ² g ⁻¹)
VCX-72	250
Ketjen black EC600	1200
Nanocyl MWCNTs	260

Table 3.8.1. Surface area of carbon materials used in this thesis.

4 | Cathodic Electrovalorisation of Furfural

The contents of this chapter have been published in two peer-reviewed journal articles: Energy & Environmental Science, and in EES Catalysis. A third article consisting of results from this chapter has been prepared and is ready for submission to a peer reviewed journal. The results of this chapter were obtained by the author of this thesis and the contributions of other people are credited in the relevant figure captions. In brief, Sihang Liu conducted all theoretical calculations in this chapter, Angus Pedersen did all ToF-SIMS experiments aided by Dr Sarah Fearn, Dr Jesus Barrio synthesised and did XPS analysis of the MTAP catalysts explained in this chapter.

4.1 Objective and Motivation

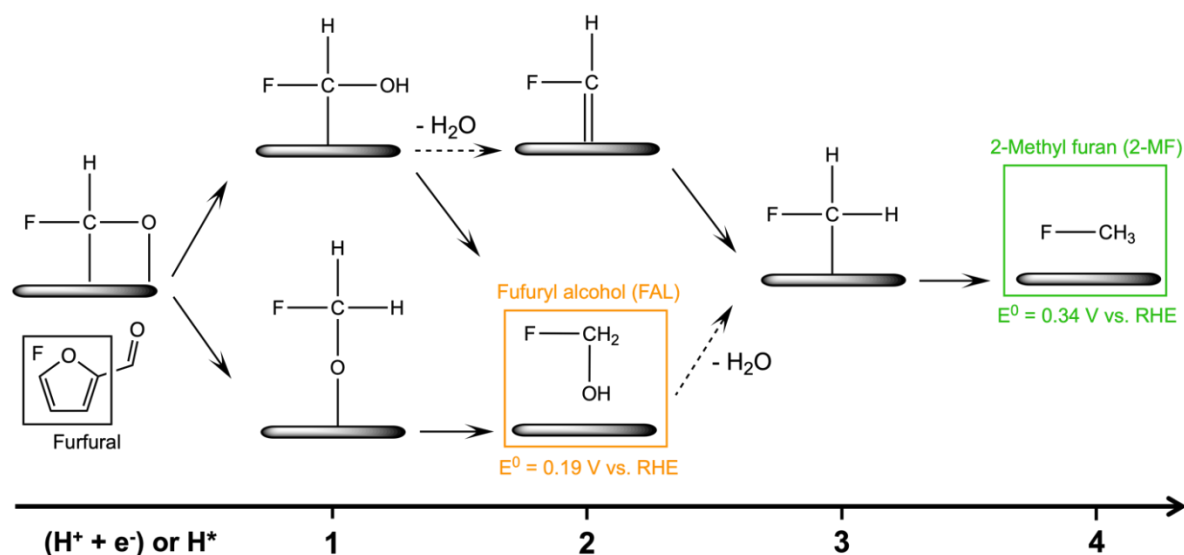
In this chapter, methods to upgrade furfural via electrochemical reduction into 2-MF, FAL, and hydrofuroin in aqueous electrolytes will be explored. All three compounds are useful products which can serve different purposes, however, the factors governing their selectivity on various electrodes are not well understood. Efforts are made to understand the fundamental reaction mechanisms which influence product selectivity which will be crucial for the development of more efficient electrocatalytic processes in the future. This section begins by exploring electrochemical furfural reduction on Cu electrodes in acidic media, which are currently the only catalysts that can produce 2-MF in significant amounts (**Figure 2.1.1**). Theoretical studies will be employed to study the intrinsic properties of Cu to elucidate what electrochemical pathways are favoured for 2-MF and FAL – the major products expected on Cu electrodes. Further experimental studies are carried out to explore the effect of other parameters such as applied potential, pH, and nature of the cation, to work out the most efficient parameters for furfural electroreduction on Cu.

Single-atom metal-organic frameworks for furfural reduction are also explored in this chapter. In recent years these catalysts have attracted a lot of attention as they exhibit good catalytic activity and selectivity in comparison to traditional metal electrodes or nanoparticles for the oxygen reduction reaction (ORR)⁶⁵ and the CO₂RR,²⁰⁴ but thus far have not been studied for other electrochemical biomass valorisations. In addition, the mechanisms which result in the corresponding reduction products have not been well explained in the literature and is where our research will be focused. Furfural reduction on copper (CuPc) and cobalt phthalocyanines (CoPc) is explored using DFT to model these catalysts. Following this, a theory-led process of producing electrocatalysts is obtained which can form the basis behind future catalyst design. Hydrofuroin is seen as the major product of these catalysts, and mechanistic studies are done to elucidate the properties which are responsible for this selectivity. These catalysts were also tested for their stability usingToF-SIMS.

The combination of DFT and experimental studies were also used to design, synthesise, and test a more diverse range of single-atom catalysts, which aimed to tune the product selectivity of the furfural reduction reaction. Fe, Cr, Co, and Ni were coordinated with nitrogen atoms by pyrolysing 2,4,6-triaminopyrimidine (TAP) to produce said catalysts. By changing the structure of the organic framework, and the nature of the central metal atom, CrTAP expressed a greater selectivity towards FAL, as opposed to hydrofuroin on the other single-atom sites, as predicted by DFT.

4.2 Furfural Reduction on Cu – What are the Dominant Pathways?

Copper electrodes are one of the most popular cathode materials that have been studied for the electrochemical reduction of furfural (**Figure 2.1.1**). Used in this context, Cu cathodes are multi-selective, being able to produce FAL, hydrofuroin, and are the only pure metal electrodes which can produce 2-MF with almost 100% selectivity but only under acidic conditions.¹⁰⁸ 2-MF is a promising biofuel which has an energy density greater than bioethanol and is comparable to gasoline.²⁰⁵ Previous attempts have been made to investigate the intrinsic properties of Cu electrodes for furfural reduction by exploring the possible mechanisms to determine intermediate species, and a rate-determining step, without much success.^{206,207} Two possible furfural reduction pathways on Cu have been proposed by Shan et al.²⁰⁸ and Chadderdon et al.¹⁰⁸ which differ in the first intermediate produced after partial reduction of adsorbed furfural (FCHO*, where * denotes an adsorbed species). FCHO* can be reduced into either FCHOH* or FCH₂O*, with these intermediates able to be further reduced into FAL or 2-MF (**Scheme 4.2.1**). The routes by which reduction can happen is either via an ECH step using adsorbed hydrogens (H*), or by a proton-coupled electron transfer (PCET) step using protons in solution. Currently, the preference for a PCET or ECH step for producing FAL and 2-MF is still disputed in the literature. Studies by Chadderdon et al.¹⁰⁸ and May et al.²⁰⁶ suggest that the ECH mechanism is dominant, by performing experiments using SAMs on Cu and Pb electrodes surface to prevent hydrogen adsorption which resulted in no production of 2-MF, and both reported that 2-MF production decreased with increasing pH.



Scheme 4.2.1. The possible pathways of the electrochemical reduction of furfural on copper electrodes.

Whilst promising, the surface poisoning experiments only confirm that the limiting steps for 2-MF and FAL production are inner-sphere reactions, and do not completely rule out pathways which directly

protonate the adsorbed furanic species. In addition, these studies as well as the findings in Chapter 2 concluded that pH is a strong determinant of what furfural reduction products are obtained on Cu, suggesting that either FAL or 2-MF production heavily relies on protons (or hydroxides) in the electrolyte rather than exclusively adsorbed hydrogens.

It has also been suggested that FAL could be an intermediate species which can be further reduced into 2-MF;²⁰⁸ however, we were able to rule this out as the intermediate species during 2-MF production by using FAL as the initial feedstock. The LSVs in **Figure 4.2.1** displayed no major difference in the current density or onset potential before and after the addition of FAL, suggesting FAL is unable to adsorb onto Cu, further supported by no 2-MF being detected after constant potential experiments at -0.50 V vs RHE. Hence, we can conclude the current densities during the LSVs are all from the HER. This was also seen by Jung et al.²⁰⁷ supporting this conclusion.

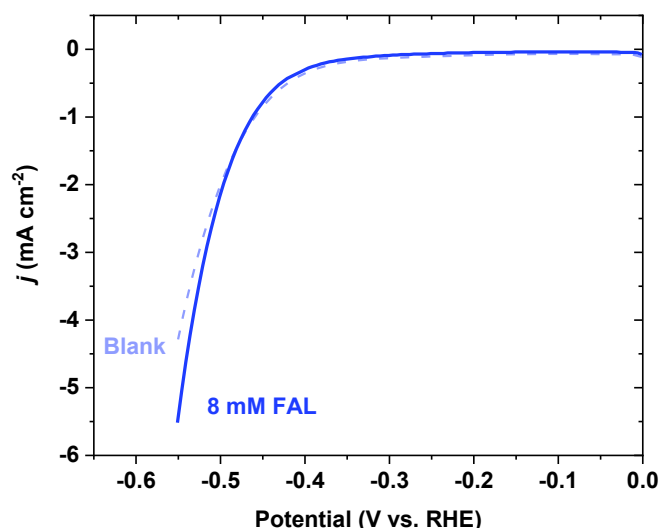


Figure 4.2.1. LSV of Cu electrodes before (dashed line) and after (solid line) the addition of 8 mM FAL. Reaction condition: 0.1 M HClO₄ electrolyte (pH 1), scan rate was 50 mV s⁻¹ and was scanned in the cathodic direction.

DFT simulations were performed to probe the possible rate-determining steps for both 2-MF and FAL production (**Figure 4.2.2**). The production of hydrofuroin was not modelled because this is an outer-sphere mechanism in acidic conditions. Despite being more thermodynamically stable, FCH₂O* is associated with a higher activation barrier compared to FCHOH*, and the -CHOH moieties prefer to bind on a 'top' site, compared to the -CH₂O in FCH₂O* binding to a 'hollow' site. The simulation predicts that FCH₂O* protonation is sterically hindered as protons from the electrolyte can have difficulty reaching the adsorbed oxygen on furfural in the hollow site, hence surface adsorbed protons can be

favourable for this reduction (ECH pathway). The free energy diagram in **Figure 4.2.2b** shows the selectivity determining step (SDS) for FAL and 2-MF. FAL is produced by FCHOH* being protonated to FCH₂OH*, or further into FCH* to make 2-MF. It is important to highlight that the second PCET step (FCHOH* protonation) has the greatest barrier during the reaction pathway at both 0 and -0.50 V vs RHE so can function as both the SDS and RDS.

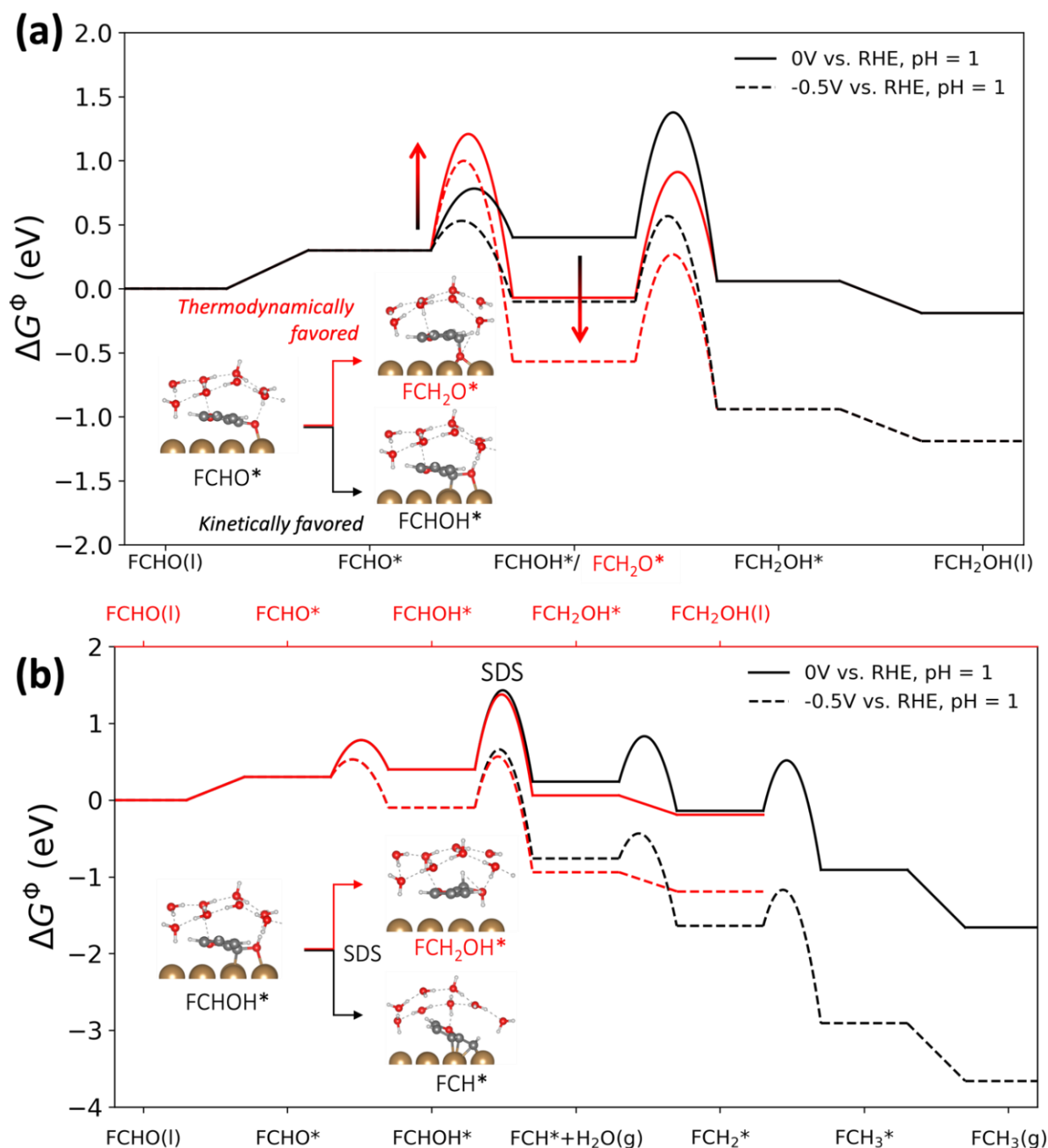


Figure 4.2.2. DFT simulation of electrochemical furfural reduction on a Cu(111) surface towards (a) FAL production and (b) 2-MF production. Both figures show the calculated routes at 0 and -0.50 V vs RHE in an acidic pH. DFT simulation was done by Sihang Liu.

Furfural reduction on Cu electrodes was explored in varying acidic pH between 0.5 and 2 (**Figure 4.2.3**). A blank LSV was performed from which the increase in current density was attributed to the HER. After the addition of 8 mM furfural, the onset potential became more anodic at each pH which signals furfural reduction, in line with similar studies which also report a lower onset potential after the addition of furfural compared to a blank electrolyte sweep,^{108,207} suggesting the activation barrier for FAL or 2-MF production is lower than that of the HER. A general trend was observed whereby the onset potential shifted slightly more anodic at lower pH which is likely an indicator that a PCET pathway is dominant, as HER requires adsorbed hydrogens because H^* is needed for both the ECH and the HER. Hence it is unlikely that furfural reduction can occur at a higher rate than HER if the ECH pathway is the dominant one.

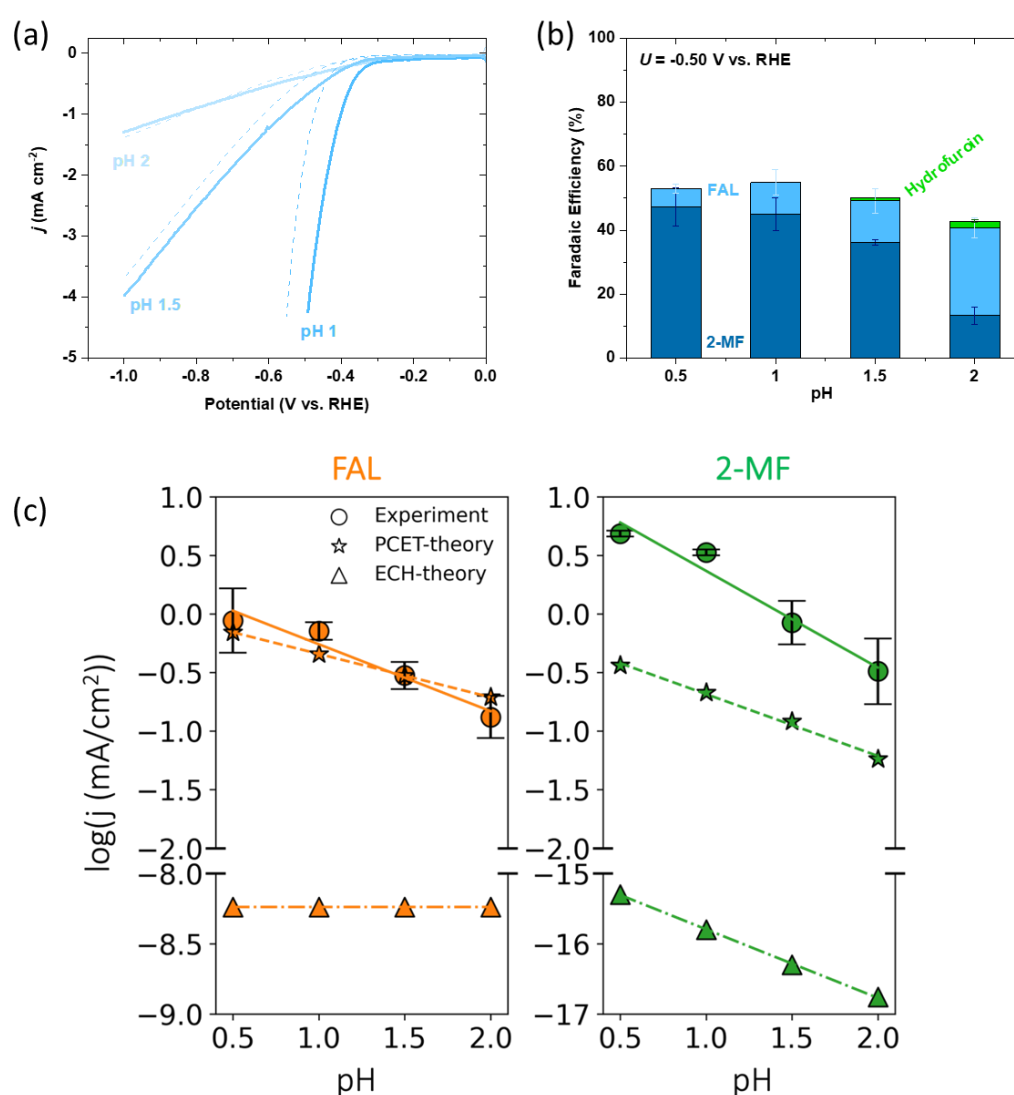


Figure 4.2.3. The electrochemical reduction of furfural and differing acidic pH. (a) LSVs of Cu electrodes before (dashed line) and after (solid line) the addition of 8 mM furfural. (b) FEs of all the liquid products obtained from furfural reduction. (c) measured and simulated partial current densities of FAL and 2-MF compared to PCET and ECH mechanisms. Reaction conditions: $HClO_4$ electrolytes, 8 mM furfural, constant potential measurements were at -0.50 V vs RHE for 3.5 hours, error bars were made from two independent experiments. The scan rate was 50 mV s⁻¹ and was scanned in the cathodic direction. DFT simulations were done by Sihang Liu.

By plotting the simulated and experimentally obtained partial current densities for 2-MF and FAL (**Figure 4.2.3c**), we can identify whether a PCET or ECH step is the most dominant pathway. H_3O^+ is assumed to be the major proton donor at these low pH levels, and in acidic conditions, PCET mechanisms tend to show a reduction in activity as pH decreases. ECH mechanisms that consume adsorbed H^* may not be as straightforward, whereby reaction parameters may have a lot of other effects. **Figure 4.2.3b** shows that a low pH is more selective towards 2-MF over FAL, with the missing current being attributed to the HER. **Figure 4.2.3c** shows that the measured partial current densities have a negative dependence on pH which is in qualitative agreement with our PCET-based simulation which shows a similar trend.

The results from the simulated ECH mechanism contrasted with the PCET with FAL production appearing pH independent across this pH range, and 2-MF showing a strong pH dependence (**Figure 4.2.3b**). The activity for ECH mechanisms towards both products is orders of magnitude lower than both the experimentally obtained data and the simulated PCET pathways (**Figure 4.2.2**). Therefore, we conclude that a PCET-based mechanism is the most dominant pathway for furfural reduction on Cu electrodes.

4.3 Cation Effect

It is possible that the nature of the cation can influence product selectivity and the rate of furfural reduction. The choice of cation during the CO_2RR affects the product selectivity, likely due to the cations providing different coordination environments to intermediate species during the reaction, which can lower activation barriers for specific products.^{209,210} To explore the effect of cations on furfural reduction, separate pH 1 HClO_4 solutions were made with Li^+ and K^+ ions added in their respective perchlorate forms along with H^+ ions used as a control (**Figure 4.3.1**).

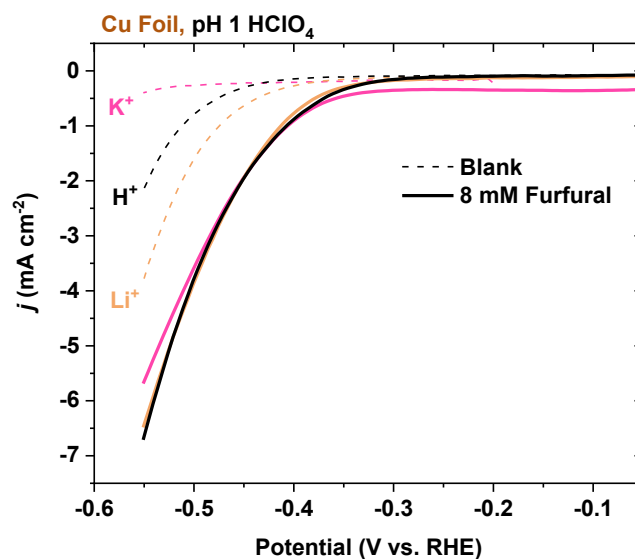


Figure 4.3.1. Linear sweep voltammograms of furfural reduction on Cu electrodes using different cations before (dashed line) and after (solid line) the addition of 8 mM furfural. Reaction conditions: 0.1 M HClO₄ electrolyte (pH 1), 50 mM KClO₄ and LiClO₄. The scan rate was 50 mV s⁻¹ and was scanned in the cathodic direction.

The LSV using Li⁺ cations displayed an earlier onset potential for the HER compared to K⁺ and the H⁺ control. However, for the furfural reduction sweeps (solid lines), changing cation from Li⁺ and K⁺ seems to not have any effect on the rate of furfural reduction or on product distribution. This could be explained by the carbonyl bond being already polarised as it is non-symmetrical, so the carbonyl bond does not need to be activated as much if at all, with any differences in products being explained by kinetic factors. Whilst the effect of cations on the HER is not completely understood, one can postulate the earlier onset for HER using Li⁺ cations is likely due to Li⁺ adsorbing on the electrode resulting in a favourable environment for the HER, possibly by providing an environment which is suitable for the adsorption and dissociation of water molecules. Conversely, K⁺ ions were shown to decrease the onset potential for the HER compared to the control. One reason for this could be due to the larger K⁺ ions forming a protective layer on the electrode surface which disrupts the HER, and a similar trend for HER activity was seen using theoretical calculation from a previous study.²¹¹

4.4 Furfural Electroreduction on Single-Atom Catalysts

In addition to 2-MF and FAL, the homocoupling of furfural results in the formation of hydrofuroin. This is the result of a radical mechanism between two furfuryl radicals that are independently formed after a single electron reduction on a cathode, which is then coupled into a C₁₀ pinacol product. Hydrofuroin has garnered attention as it can undergo ring-opening reactions and deoxygenations to produce straight-chain hydrocarbons that can be used as jet fuels.^{126,128} Existing catalysts which electrochemically produce hydrofuroin use Pb^{107,108} or Al,⁹⁶ however, these electrodes have toxicity issues, report significant amounts of FAL along with hydrofuroin, and use relatively high overpotentials for this conversion.

Single-atom molecular catalysts (catalysts where the metal centre acts as the active site) are a promising alternative to standard metal electrodes. The main advantages of these electrocatalysts were described in **section 1.4**. Examples of single-atom catalysts include metal phthalocyanines such as cobalt (CoPc) and copper phthalocyanine (CuPc), where the central metal atom is coordinated with four nitrogen atoms. These compounds have previously been shown to electrochemically reduce CO₂ into syngas, with minor amounts of C₂₊ products in alkaline electrolytes.²¹² It is worth noting that this reaction occurs at similar potentials to furfural reduction (-0.50 to -1.0 V vs RHE) and both involve the cleavage of a C=O.⁶⁷ From this, it can be hypothesised that the carbonyl bond on furfural may also be reduced on these single atom sites at similar potentials. Furthermore, as Cu is the only monometallic electrode that can produce C₂₊ products during the CO₂RR,^{213,214} hydrofuroin may potentially be produced in good quantity as a coupled product using CuPc decorated cathodes. A depiction of the reaction setup and calculated equilibrium potentials of furfural reduction products are shown in **Figure 4.4.1**.

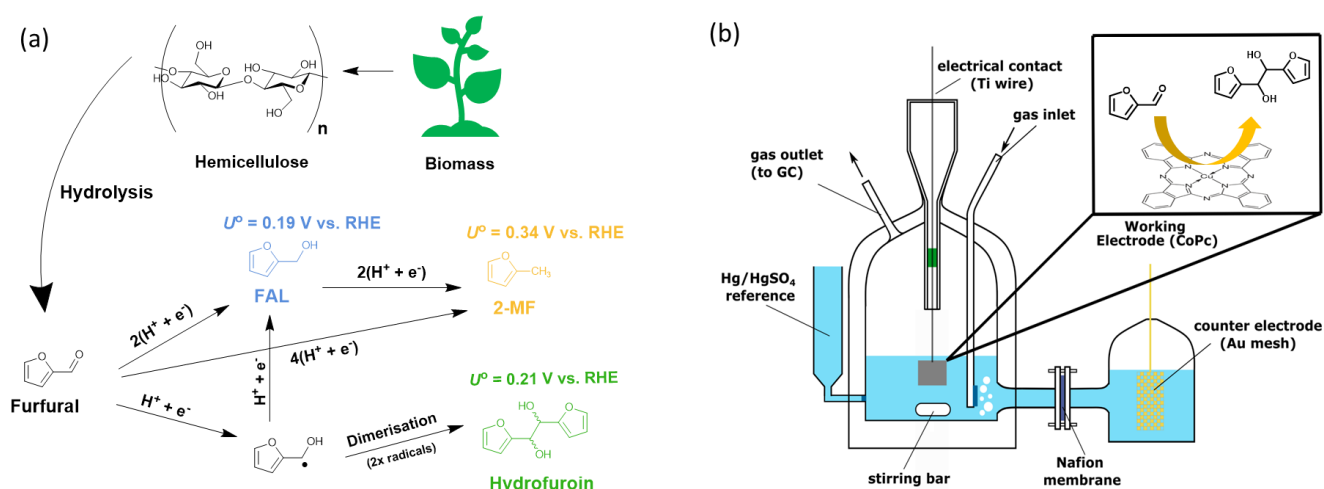


Figure 4.4.1. The electrochemical reduction of furfural using CoPc. (a) Pathways of producing furfural reduction products and their calculated equilibrium potentials. Equilibrium potentials were calculated by Sihang Liu. (b) The electrochemical setup used for this reaction.

4.5 Theoretical Understanding of Furfural Reduction

Previous studies⁷⁹ proposed a route for hydrofuroin synthesis which suggested two PCET steps producing the furfuryl radicals on the electrode surface, which were able to couple with each other in later steps depicted in the equations below. We were able to calculate a free energy diagram (**Figure 4.5.1a**) depicting the formation of hydrofuroin at -0.50 V vs RHE using simulated CoPc, CuPc, graphene, and Pb(111) surfaces. It was determined that the first PCET step to produce FCHOH* from FCHO* is still potential determining at -0.50 V vs RHE, and when comparing the limiting potentials of CoPc, CuPc, and Pb with graphene, it indicates that the single-atom catalysts should achieve a current density for hydrofuroin formation at less cathodic overpotentials than pure graphene, highlighting the significance of the central metal atom. It is also important to note that the FCHOH* intermediate seems to be unstable on these surfaces so is likely to desorb, suggesting that the coupling reaction could occur in solution opposed to the electrode surface.

- | | |
|--|--------------------------|
| 1. $2\text{FCHO (l)} + 2* \leftrightarrow 2\text{FCHO}^*$ | Furfural adsorption (x2) |
| 2. $2\text{FCHO}^* + 2(\text{H}^+ + \text{e}^-) \leftrightarrow 2\text{FCHOH}^*$ | PCET (x2) |
| 3. $2\text{FCHOH}^* \leftrightarrow \text{Hydrofuroin } * + *$ | Coupling reaction |
| 4. $\text{Hydrofuroin}^* \leftrightarrow \text{Hydrofuroin (l)}$ | Hydrofuroin desorption |

Where * represents an unoccupied active site.

A separate plot which could predict furfural reduction products was made using the adsorption energies of furfural and hydrogen as simple descriptors (**Figure 4.5.1b**), which was inspired by a previous study on product classification of the CO₂RR.⁶¹ **Figure 4.5.1b** shows that stronger binding materials such as Ru and Rh are likely to produce purely H₂, whereas a moderate binding surface is selective towards 2-MF, with minor amounts of FAL which is encouraging as this product distribution was seen in the previous section for furfural reduction on Cu electrodes. When plotted, CoPc, CuPc, Pb, and graphene all display weak binding energies for both descriptors and report hydrofuroin as the main organic product. The weak binding of the metal phthalocyanines could be due to furfural only binding to the central atom, and not the more intimate adsorption involving the furan ring compared to metal surfaces.

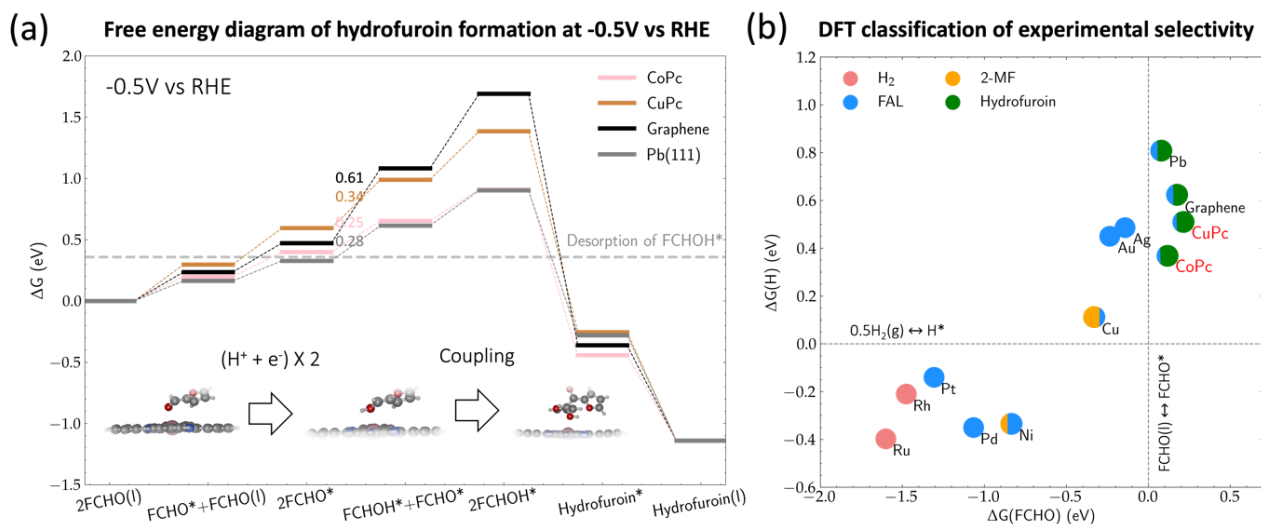


Figure 4.5.1. Theoretical studies of the furfural reduction reaction. (a) free energy diagram of hydrofuroin formation on CoPc, CuPc, graphene, and Pb(111) at -0.50 V vs. RHE. (b) Predicted experimental selectivity of furfural reduction products on various surfaces. DFT simulation was done by Sihang Liu.

To test this concept, the optimised furfural adsorptions were simulated on graphene-supported CoPc, CuPc, Co(0001), and Cu(111) and are denoted in **Figure 4.5.2**. The simulations revealed possible explanations for the weak binding energies between furfural and the single-atom catalysts. On phthalocyanines, only the -CHO group in furfural interacted with the central metal atom, whereas the entirety of the atoms in furfural appeared to interact with the monometallic surfaces. An initial summary suggests that surfaces which are more selective towards hydrofuroin fall into the weak binding regions, and the reaction could be limited by the FCHO^* to FCHOH^* protonation.

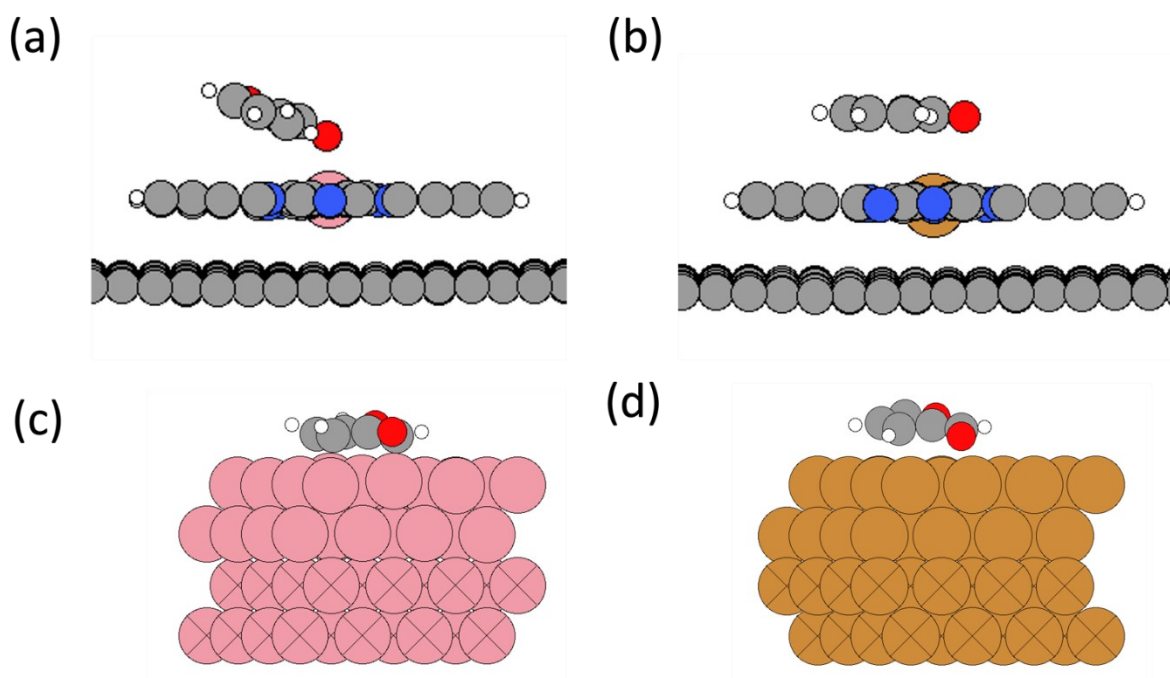


Figure 4.5.2. Optimised furfural adsorption modes on (a) CoPc, (b) CuPc, (c) Co(0001) and (d) Cu(111). The CoPc and CuPc are both graphene supported. Key: pink – cobalt, brown – copper, grey – carbon, blue – nitrogen, white – hydrogen, red – oxygen. Credit Sihang Liu.

4.6 Electrochemical Activity of Furfural Reduction Catalysts

Following these calculations, the catalytic activity of CoPc and CuPc towards furfural reduction was explored. To improve their conductivity, both catalysts were physisorbed onto multi-walled carbon nanotubes following the synthesis procedure of Zhang et al.,⁶⁷ and the catalysts deliberately had a low wt/wt% of metal atoms (around 1.21-1.65%, confirmed by XPS, **Figure 4.6.1c**) to avoid metal cluster formation. HAADF-STEM and EDX were used to confirm the presence of single Cu atoms on the CuPc catalyst and showed only minor clustering before electrochemistry (**Figure 4.6.1b**). A mildly basic (pH 10) potassium bicarbonate buffer was used as the electrolyte as metal phthalocyanines are unstable in acidic conditions, and furfural rapidly degrades in very alkaline media (>pH 13).²¹⁵ **Figure 4.6.1a** shows the LSVs of CoPc and CuPc electrodes compared to a carbon black control, before and after the addition of 8 mM furfural. Both metal phthalocyanines displayed an onset potential less cathodic than the carbon black control as predicted from DFT. When compared to the current state-of-the-art Pb electrodes, CuPc and CoPc display onset potentials that are ~40 and ~130 mV less cathodic respectively, signifying a major advantage to using these materials.

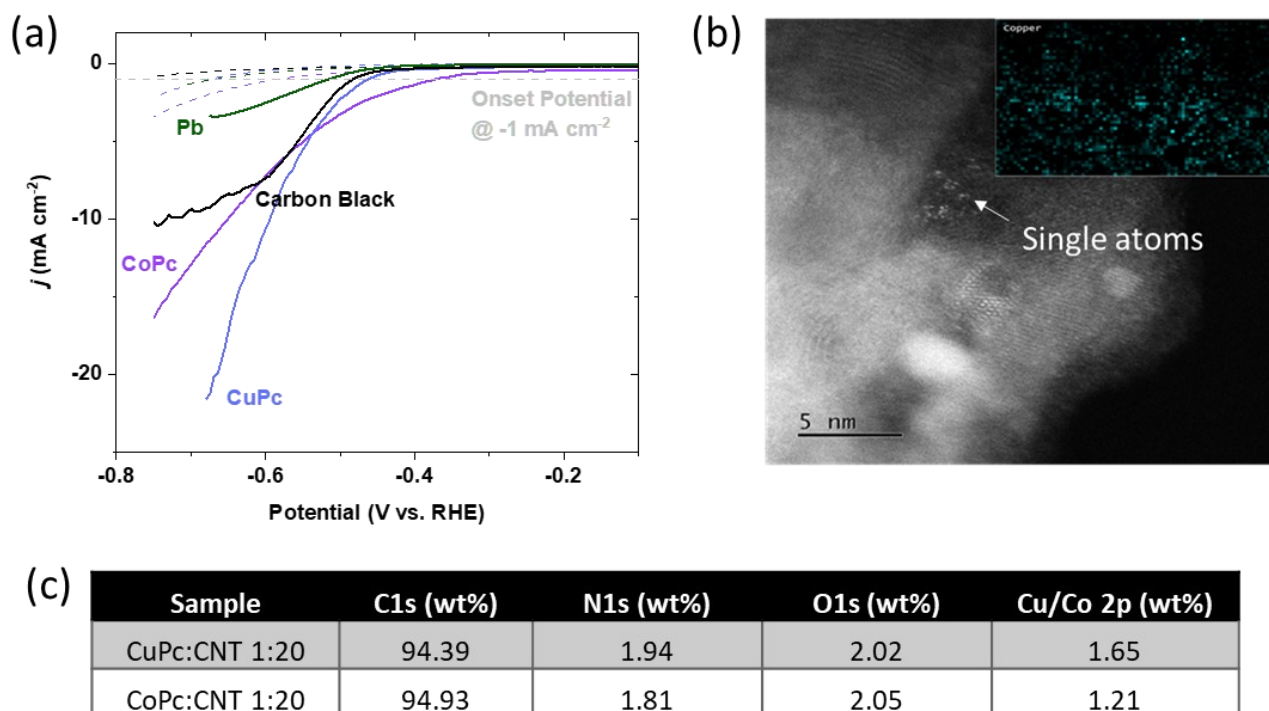


Figure 4.6.1. Synthesis and characterisation of single-atom catalysts. (a) Comparisons of furfural reduction onset potentials. LSVs of Pb, CoPc, CuPc, and carbon black electrodes before (dashed line) and after (solid line) the addition of furfural. (b) HAADF-STEM and EDX image of synthesised CuPc catalysts, depicting single copper atoms. The image was taken by Dr Alain Li. (c) Table showing the calculated wt/wt% of CuPc and CoPc catalysts calculated using XPS. Reaction conditions: 0.1 M potassium bicarbonate-carbonate buffer (pH 10), 8 mM furfural, catalyst loading 0.1 mg cm⁻². The scan rate was 50 mV s⁻¹ and was scanned in the cathodic direction.

After chronoamperometry for 1 hour at -0.50 V vs RHE, product quantification revealed that hydrofuroin was indeed the main product on both the metal phthalocyanines, Pb, and the carbon control, as predicted from our theoretical selectivity map in **Figure 4.5.1b**. The quantified products (**Figure 4.6.2b & c**) revealed that the pure carbon electrode produced hydrofuroin, but with lower electrochemical activity compared to the phthalocyanines. In addition, there was more unaccounted-for charge when using the carbon electrode, which is explained by the unidentifiable peaks in the HPLC chromatograms and is likely humin products resulting from unselective radical coupling. These are reported as 'Other' in **Figure 4.6.2c**. Fewer humin products were detected on CuPc and CoPc, indicating that the central metal atom could provide a key reaction site to where the carbonyl bond can ligate, which explains the increase in current density and fewer amounts of unselective radical coupling.

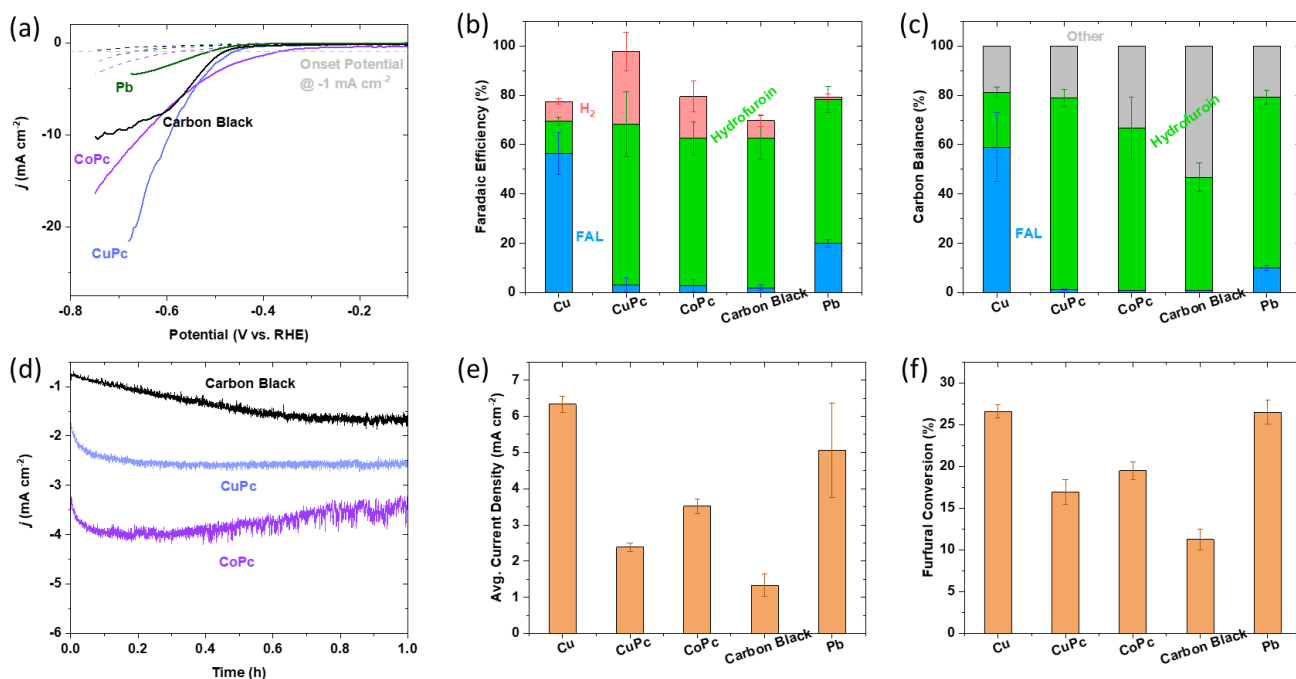


Figure 4.6.2. The electrochemical activity of different cathode materials for furfural reduction. (a) LSVs of CoPc, CuPc, Pb, and carbon black control before (dashed line) and after (solid line) the addition of 8 mM furfural. (b) Faradaic efficiencies and (c) carbon balance of detected products after chronoamperometry experiments. (d) Chronoamperometry, (e) average current density, and (f) furfural conversion obtained after constant potential experiments. Reaction conditions: 0.1 M potassium bicarbonate-carbonate buffer (pH 10), 8 mM furfural, carbon catalyst loading was 0.1 mg cm⁻², applied potential was -0.50 V vs RHE for 1 h. The scan rate for the LSVs was 50 mV s⁻¹ and was scanned in the cathodic direction.

The effects of other parameters affecting furfural reduction on the phthalocyanines were also explored including varying overpotentials and initial furfural concentration on both CoPc and CuPc. **Figure 4.6.3a & b** depict the products obtained between -0.40 and -0.70 V vs RHE for each catalyst. A general trend for both materials is seen whereby at more cathodic potentials, hydrofuroin is produced in greater amounts along with the lower formation of FAL and H₂. This was attributed to greater rates of furfural adsorption and electron transfer, leading to the greater rate of formation of furfuryl radicals and subsequent greater radical coupling towards hydrofuroin. CuPc produced fewer humin products than CoPc, which is likely due to greater radical stability provided on Cu atoms, compared to other metals, which was also seen in previous studies.¹²²

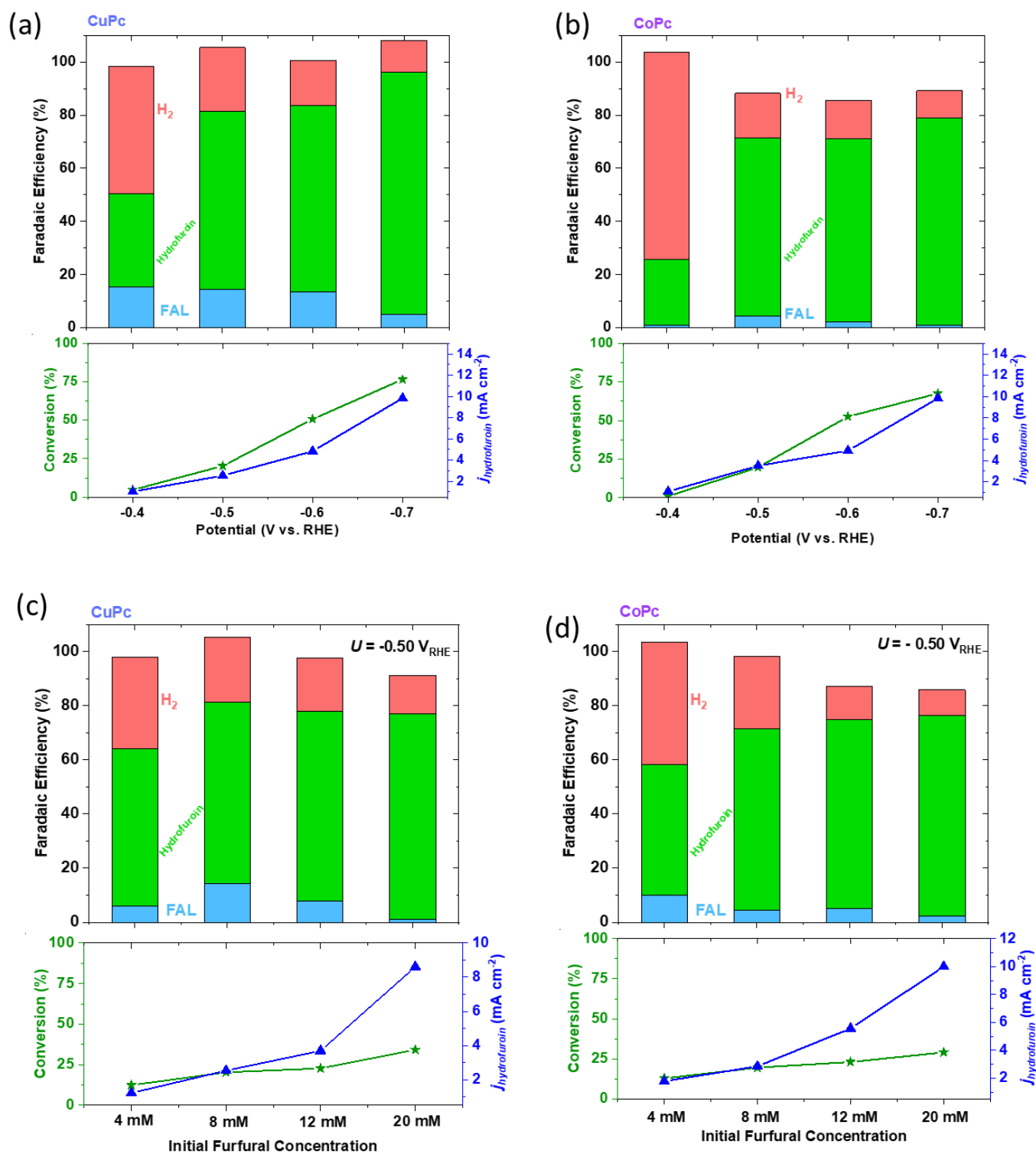


Figure 4.6.3. Electrochemical reduction of furfural on CoPc and CuPc cathodes. Faradaic efficiencies, furfural conversion, and partial current densities of hydrofuroin at varying potentials on (a) CuPc and (b) CoPc. Faradaic efficiencies, furfural conversion, and partial current densities of hydrofuroin from varying initial furfural concentrations on (c) CuPc and (d) CoPc. Reaction conditions: 0.1 M potassium bicarbonate-carbonate buffer electrolyte (pH 10), varying potential experiments used 8 mM furfural, varying initial concentration experiments were done at -0.50 V vs RHE. All potentials were held for 1 h and catalyst loading was 0.1 mg cm^{-2} .

Radical couplings are generally hard to control, however, it can be hypothesised that a low initial concentration of furfural may aid in lowering rates of unselective coupling to form the long-chained oligomers. To study this effect, experiments, whereby the initial concentration of furfural was varied, were carried out at a fixed potential of -0.50 V vs RHE on both phthalocyanines. **Figure 4.6.3c & d** show the FEs of the products at different concentrations of initial biomass ranging from 4 to 20 mM. On both catalysts, at higher concentrations, the selectivity for hydrofuroin increases, and the amount of FAL and H_2 steadily decreases. This is rationalised by having a greater concentration of furfuryl radicals produced at higher concentrations as well as higher rates of furfural adsorption. This also explains the lower levels of the HER because there are now fewer active sites for hydrogen adsorption, and by extension, lower rates of FAL production, as the Volmer step needed for this pathway is essentially suppressed. It must be noted however that on both CoPc and CuPc, with increasing initial furfural concentration the amount of unaccounted charge increases as does the amount of unidentifiable organic products. This suggests that at high concentrations of furfural, there are more unselective radical couplings which produce humins. CuPc shows slightly less unaccounted total charge than CoPc but the total current density is lower compared to at higher concentrations of furfural. This is an important factor to consider when scaling up hydrofuroin synthesis, as too many humin products can poison the electrocatalyst and reduce efficiency, but a too low concentration will result in poor electrochemical activity.

The electrochemical hydrofuroin production was tested over an extended period of 5 h using CoPc (**Figure 4.6.4**). CoPc was chosen for extended-time measurements because it showed the highest current densities at -0.50 V vs RHE and displayed the highest selectivity towards hydrofuroin. As the experiment progressed, hydrofuroin was found to increase linearly over time, suggesting a first-order dependent mechanism with low amounts of FAL also produced. A gradual decrease in the current density was seen which is likely to be mainly due to greater amounts of furfural consumption over time.

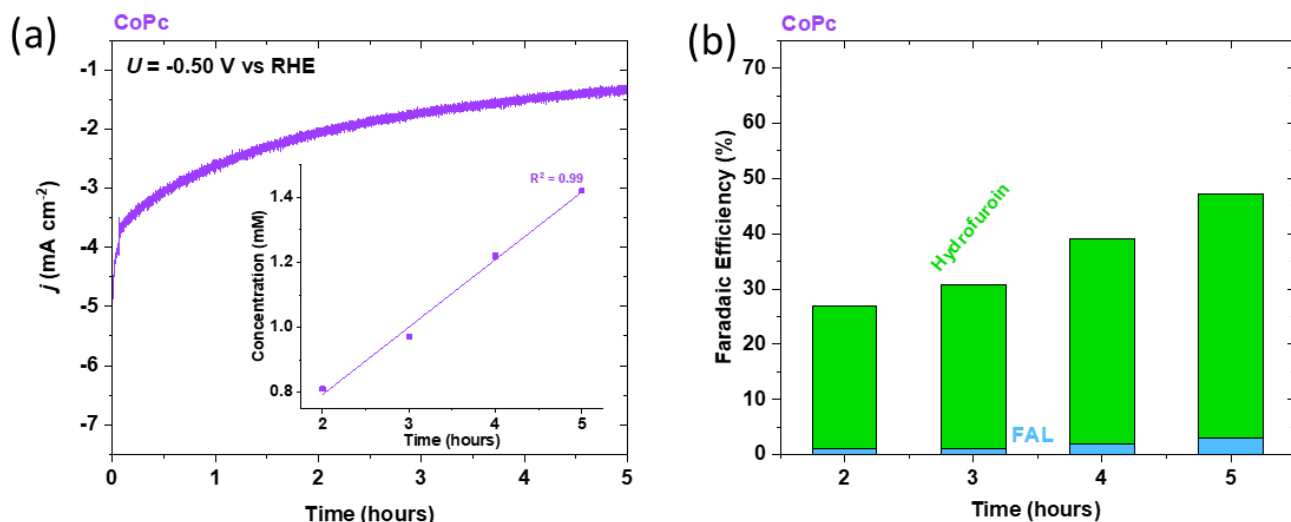


Figure 4.6.4. Extended-time electrolysis for furfural reduction on CoPc. (a) Chronoamperometry over 5 h. Insert graph showing the concentration of furfural produced per hour suggesting a first-order reaction. (b) Faradaic efficiencies of detected liquid products per hour. Reaction conditions: 0.1 M potassium bicarbonate-carbonate buffer (pH 10), catalyst loading 0.10 mg cm⁻², -0.50 V vs RHE for 5 h, 8 mM furfural.

Maximum turnover frequencies (TOFs) for CoPc and CuPc for hydrofuroin production were calculated using the method of Mehmood et al.²¹⁶ Assumptions were made whereby each metal atom was assumed to be an active site available on the surface of the electrode, and the number was determined using the wt/wt% from XPS. The minimum site density was calculated using **equation 4.1** where A_r is the relative atomic mass and N_A is Avogadro's number (6.023×10^{23}). TOFs were calculated using **equation 4.2** where j_{HF} is the partial current density of hydrofuroin per gram of catalyst and e is the charge of an electron. The TOF is a maximal estimate because the calculated site density is a minimum. The TOFs at -0.50 V vs RHE using 8 mM furfural were 0.40 ± 0.10 and 0.35 ± 0.01 electrons/site⁻¹ s⁻¹ for CoPc and CuPc respectively.

$$\text{Min. Co Site Density [sites g}^{-1}\text{]} = \text{wt\%}(\text{Co})/A_r(\text{Co})[\text{g mol}^{-1}] \times N_A [\text{sites mol}^{-1}] \quad \text{Eqn. 4.1}$$

$$j_{HF} [\text{A g}^{-1}] = e [\text{C electron}^{-1}] \times \text{TOF} [\text{number of electrons}/2 \text{ site}^{-1} \text{ s}^{-1}] \times \text{SD} [\text{site g}^{-1}] \quad \text{Eqn. 4.2}$$

4.7 Stability of CuPc and CoPc

The group of Jaramillo²¹⁷ had previously used ToF-SIMS to confirm the presence of single Ni sites for the CO₂RR, however, they did not do any measurements post chronoamperometry. A new level of novelty was added whereby ToF-SIMS was used to probe the stability of the single-atom molecular catalysts by comparing fragments before and after one hour of chronoamperometry at -0.50 V vs. RHE. **Figure 4.7.1** shows the results of normalised counts of Cu/CoPc and shows the counts of CoPc and CuPc decrease by 16% and 67% respectively, indicating the greater stability of CoPc compared to CuPc. It must be noted that the Co₂N₃C₃ fragment has previously been reported to originate from μ -cyano bridged CoPc dimers.²¹⁸ For CuPc, a 67% and 69% reduction in Cu⁺ and CuPc⁺ normalised counts were observed, suggesting that CuPc may be removed from the surface of the electrode during chronoamperometry, and the lower stability of CuPc is in line with previous studies on CuPc showing that they tend to aggregate and deviate away from the phthalocyanine structure under reducing conditions due to its high surface energy.²¹⁹ The formation of Cu nanoparticles can also explain the increased amounts of FAL seen on CuPc compared to CoPc which has been seen in previous studies.^{219–}

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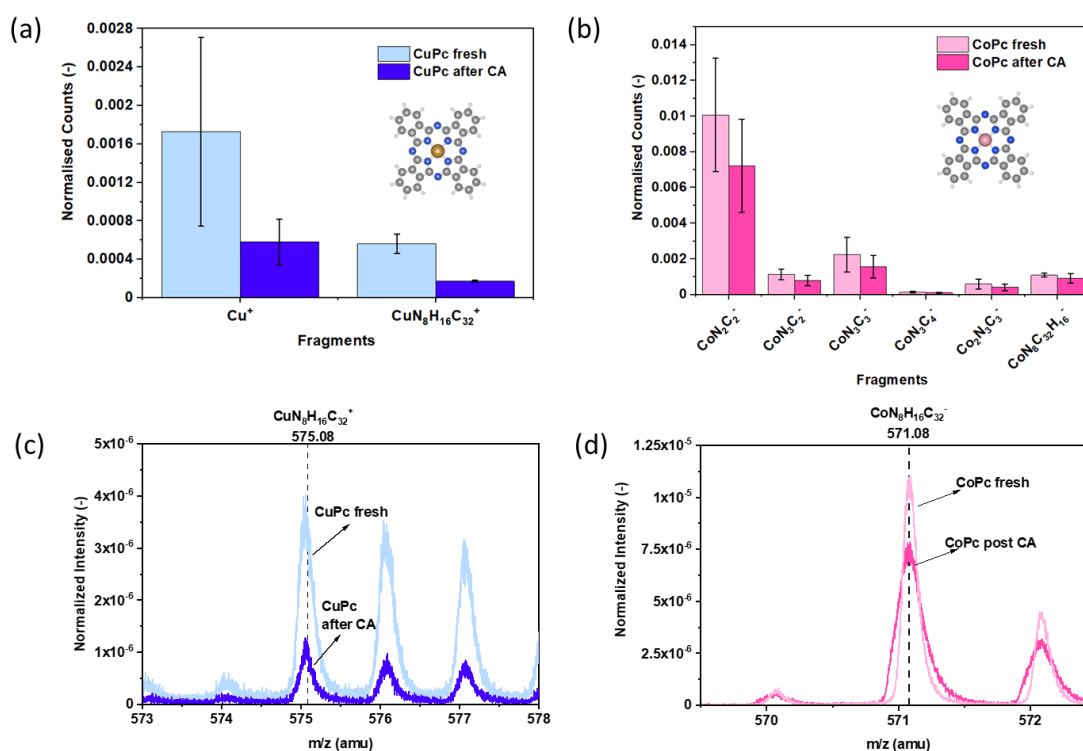


Figure 4.7.1. Positive ToF-SIMS results of (a) CuPc and (b) CoPc before and after chronoamperometry at 0.50 V vs RHE for 1 hour. Fragment counts were normalised to the total ion count, and error bars were produced from four measurements in separate locations. Reaction conditions: 0.1 M potassium bicarbonate-carbonate buffer (pH 10), 8 mM furfural, -0.50 V vs RHE for 1 hour, catalyst loading was 0.4 mg cm⁻². ToF-SIMS was carried out by Angus Pedersen.

Since CoPc showed the highest stability and highest currents of the carbon-based catalysts, a further test was established to determine the reusability of the catalyst. A fresh electrolyte was prepared, and furfural reduction was conducted at -0.50 V vs RHE for one hour. After the catalyst was rinsed with MilliQ water a fresh electrolyte was prepared and furfural reduction was done again using the same CoPc electrode. **Figure 4.7.2** shows the LSVs and chronoamperometry of the fresh electrode and reused electrode, with both the LSV and chronoamperometry showing only a minor loss in current densities, which confirms that CoPc is relatively stable under these reaction conditions.

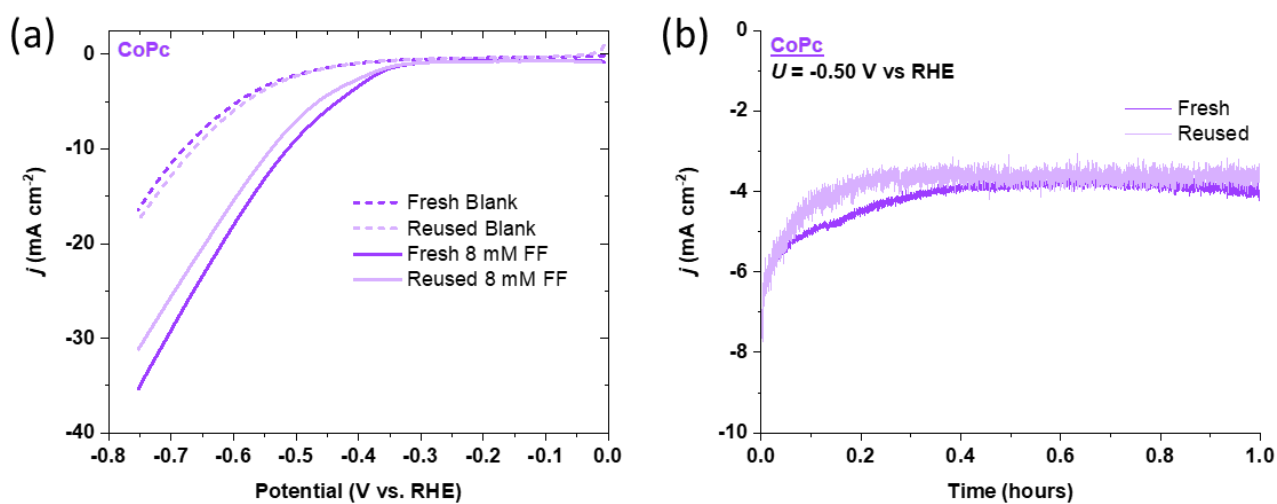


Figure 4.7.2. Reusability test of CoPc for furfural reduction. (a) LSV of CoPc before (dashed line) and after (solid line) the addition of furfural on fresh and reused CoPc electrodes. (b) Chronoamperometry measurements of fresh and reused CoPc electrode. Reaction conditions: 0.1 M potassium bicarbonate-carbonate buffer (pH 10), catalyst loading was 0.1 mg cm⁻², 8 mM furfural, constant potential set at -0.50 V vs RHE. The scan rate for the LSVs was 50 mV s⁻¹ and was scanned in the cathodic direction.

4.8 Proposed Mechanism of Hydrofuroin Production

To delve deeper into the mechanisms surrounding electrochemical hydrofuroin production, a comparison of the partial current densities of hydrofuroin at different initial furfural concentrations was taken. From this, a first-order dependence concerning initial furfural concentration was observed for both CoPc and CuPc (**Figure 4.8.1a**). This suggests that the RDS is likely the radical formation (first PCET step) as opposed to a radical coupling which would result in a second-order dependence, with coupling occurring on the electrode surface. By extension, this also means that a first-order dependence would result in the furfuryl radical being desorbed as soon as it is produced and will couple in solution to form hydrofuroin, which was found to be thermodynamically feasible according to **Figure 4.5.1b**, i.e., this step shows the protonation step for FCHO^* to FCHOH^* is the only endothermic step. This hypothesis is further supported from the HPLC chromatogram in **Figure 4.8.1b** where the two hydrofuroin isomers have an almost equal concentration. We would expect a difference in isomer distribution for surface-level coupling on an assumed flat surface electrode. This factor was observed on Cu electrodes where the minor amounts of hydrofuroin produced display a $\sim 3:1$ isomer distribution (brown line, **Figure 4.8.1b**). The theory of radical coupling in solution is not too farfetched as a recent study was published and managed to detect the furfuryl radical in solution using EPR combined with DFT for the furfural reduction on Pb electrodes in acidic media.¹⁰⁷ In conclusion, combining both the experimental and theoretical data, the main factor which determines hydrofuroin production on these catalysts is the first PCET step, as opposed to any coupling steps.

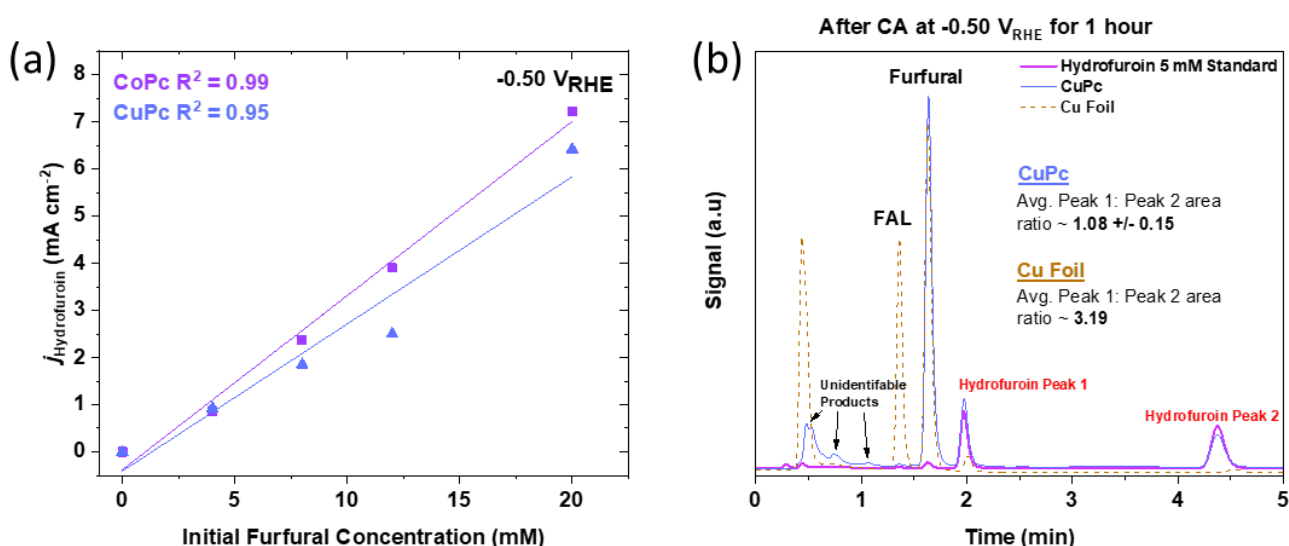
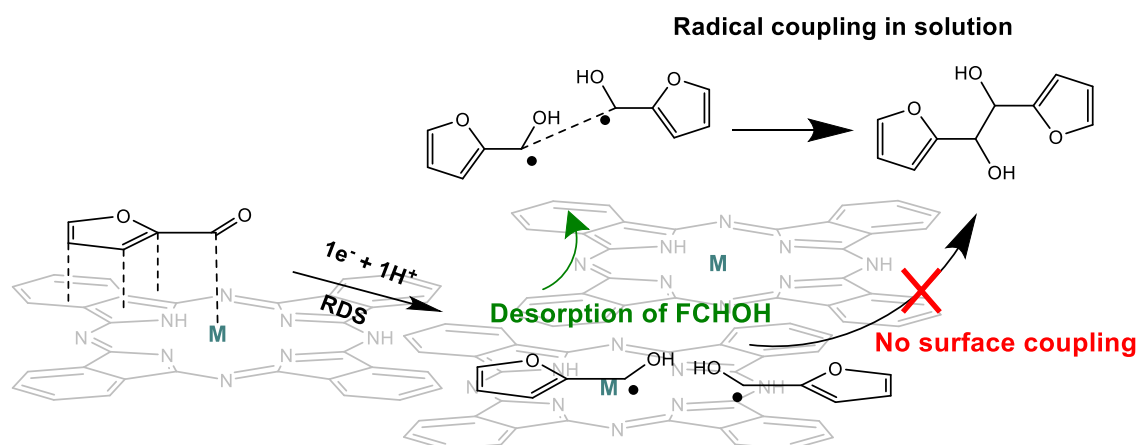


Figure 4.8.1. Mechanistic study for the electrochemical production of furfural. (a) Partial current densities of hydrofuroin production at different initial furfural concentrations. (b) HPLC chromatograms comparing 5 mM standard solution of hydrofuroin with the electrolyte after chronoamperometry experiments on CuPc and Cu

foil. For the minor amounts of hydrofuroin produced on Cu foil, a disproportionate amount of one isomer is preferred. Reaction conditions: 0.1 M potassium bicarbonate-carbonate buffer (pH 10), 4-20 mM furfural, potential applied for all experiments was -0.50 V vs RHE for 1 hour, catalyst loading was 0.1 mg cm⁻².

After collating the data from the above experiments, a reaction mechanism can be proposed (**Scheme 4.8.1**) for the electrochemical production of hydrofuroin on metal phthalocyanines. Assuming that each phthalocyanine molecule is a flat surface, there are potential avenues towards a stereoselective electrosynthesis if the framework is tuned to force a second-order dependence concerning the furfuryl radical. This would require the phthalocyanine to not desorb the radical once it is produced, which may be possible by either changing the identity of the metal atom or editing the framework with moieties which are electron donating or withdrawing.



Scheme 4.8.1. Proposed mechanism of hydrofuroin formation during the electrochemical reduction of furfural on metal phthalocyanines. 'M' represents a metal atom or ion.

The selectivity mapping that was produced in **Figure 4.5.1b** is significant as it offers a basic outline for designing other electrocatalysts which can have their binding energies towards furfural and hydrogen tuned, to be selective towards other products such as 2-MF and FAL. An example of this may include changing the nature of the metal atom, or the nature of the framework which is discussed in the next section.

4.9 Can we steer Selectivity Away from Hydrofuroin?

Aside from metal porphyrins and phthalocyanines, other metal-organic frameworks have been synthesised that show activity for use in hydrogen evolution,²²² nitrate reduction^{223,224} and for the CO₂RR.²²⁵ In the previous section, a theoretical selectivity map was made comparing the binding energies of furfural and hydrogen which showed that single-atom molecular catalysts are predicted to be selective towards hydrofuroin, due to the calculated weak binding energies of Co and CuPc with furfural and hydrogen. The validity of this mapping was later confirmed by experiments where it was shown that hydrofuroin was indeed the major product of electroreduction on the single atoms, as well as Pb, carbon, and copper electrodes whose binding energies were also calculated. An extension of this theory-based catalyst synthesis is explored in this section whereby the binding energies between single-atom catalysts and furfural/hydrogen are attempted to be tuned to affect product selectivity. One of the simplest ways this can be done is by altering the nature of the central metal atom to Earth abundant metals such as Fe, Co, Cr, and Ni, coordinated by four nitrogen atoms (MN₄C catalysts).

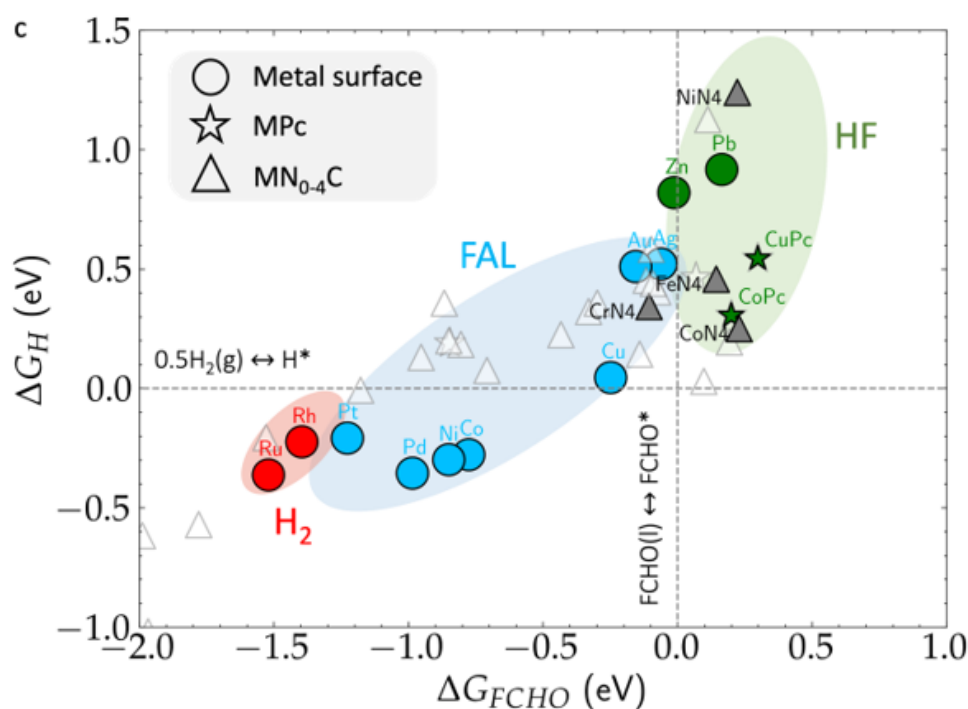


Figure 4.9.1. Selectivity mapping for furfural reduction products using furfural and hydrogen adsorption energies as descriptors. DFT simulation was done by Sihang Liu.

Figure 4.9.1 shows a selectivity map of simulated new MN₄C catalysts alongside the CoPc and CuPc systems used in **section 4.5**, comparing the adsorption energies of furfural and hydrogen. The phthalocyanines and Ni-, Fe-, and CoN₄ catalysts all display the weak binding energies associated with hydrofuroin production, but interestingly the CrN₄ catalyst has binding energies comparable to Cu and

Ag. These binding energies should lead towards FAL as a preferred furfural reduction product. To confirm the validity of the theory, Ag electrodes were tested for their furfural reduction capability at pH 10. The LSVs (**Figure A3**) show an increase in current density and an earlier onset potential once furfural was added, with FAL being detected as the main liquid product detected with 65.4% FE at -0.50 V vs RHE, with minor amounts of hydrofuroin (13.7% FE). This result in turn should add validity to CrN₄ catalysts being able to produce increased amounts of FAL because they are both in similar adsorption regions.

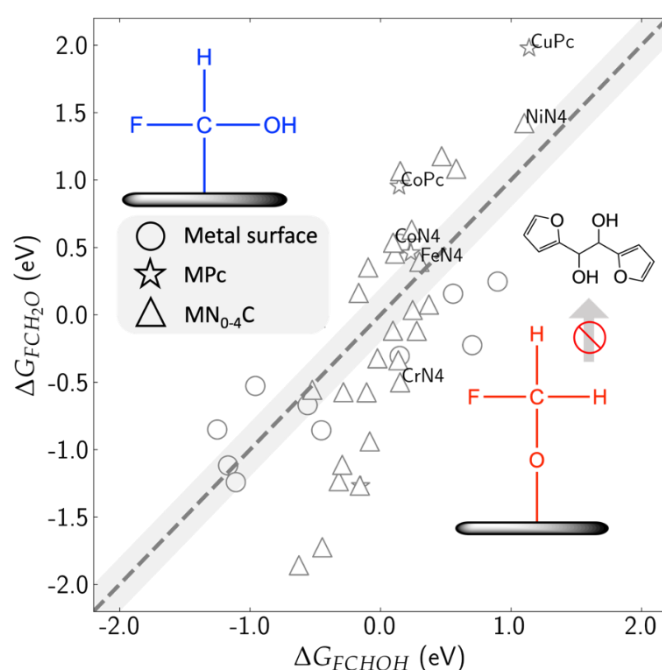


Figure 4.9.2. The relative stability of FCHOH* and FCH₂O* intermediates modelled on different catalyst surfaces. DFT simulation was done by Sihang Liu.

In the previous section regarding furfural reduction on Cu, **Figure 4.2.2** suggested the FCHOH* intermediate is the preferred pathway towards hydrofuroin, whereas the FCH₂O* is the intermediate that leads to FAL production. **Figure 4.9.2** shows the relative stability of both intermediates over different catalysts, highlighting all the catalysts used in the previous section and the MN₄ catalysts to be tested in this study. Most of the single-atom catalysts display a preference towards the FCHOH* intermediate, therefore a preference for hydrofuroin as the main reduction product (**Figure 4.5.1**). However, CrN₄C shows that it favours the FCH₂O* intermediate suggesting the thermodynamic pathway towards hydrofuroin is hindered, and FAL is preferred instead.

After determining that by changing the nature of the central atom it could theoretically be possible to steer the binding energies away from the hydrofuroin selectivity region (**Figure 4.9.1**), a series of MN_4C catalysts were synthesised. Each MN_4C catalyst was synthesised through a two-step process coordinating each metal ion using 2,4,6-triaminopyrimidine (TAP) to produce the respective ‘MTAP’ catalyst where M represents a metal atom, following the synthesis method reported previously by Barrio et al.⁶⁵ The synthesis procedure of these catalysts and XPS characterisation for CrTAP and CoTAP is shown in **Figure 4.9.3b & c**. Further characterisation of these catalysts is underway.

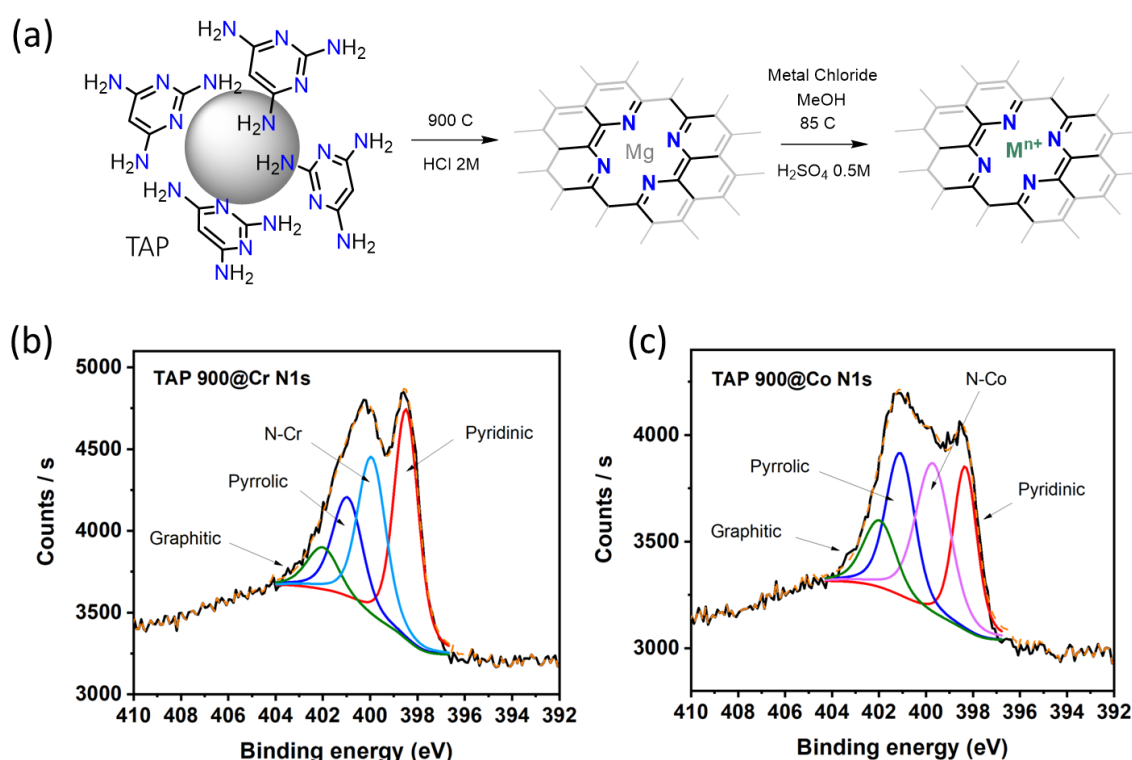


Figure 4.9.3. Synthesis of MTAP catalysts. (a) Scheme of Mg templated MTAP production. N1s core level XPS spectra of (b) CrTAP and (c) CoTAP. Credit: Jesus Barrio for synthesis and characterisation.

The synthesised MTAP catalysts were tested for furfural reduction activity in a pH 10 bicarbonate-carbonate buffer, taking a blank LSV before and after the addition of 8 mM furfural. The current of the blank sweep was attributed to the HER, and after the addition of furfural, the LSV showed an anodic shift in the onset potential on Fe-, Co- and CrTAP. The LSV on NiTAP did not shift, suggesting that furfural reduction may not be limited on this catalyst. Chronoamperometry measurements for each catalyst were done at -0.50 V vs. RHE for one hour, and the liquid products were detected using HPLC. **Figure 4.9.4f** shows that all the single atoms produced good amounts of hydrofuroin as the main

organic product, the most selective being with CoTAP with 73.4% FE. As predicted from DFT, CrTAP produced significantly more FAL (16.1% FE) than the other catalysts (0.1 – 3.7% FE), with FAL partial current densities much higher than the others, likely due to the FCH_2O^* intermediate being more thermodynamically feasible, whereas the hydrofuroin produced on CrTAP could be from a more kinetically favoured pathway.

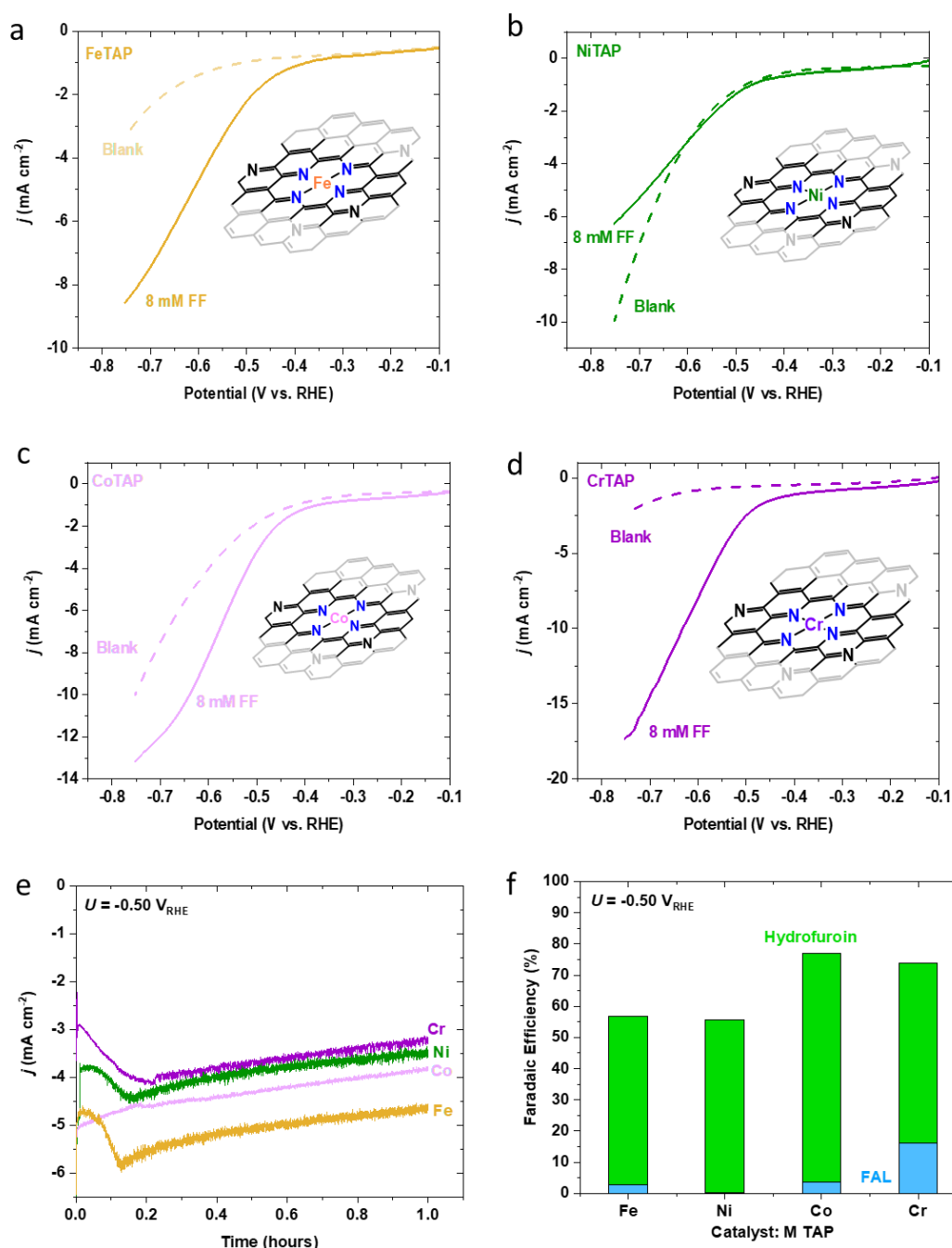
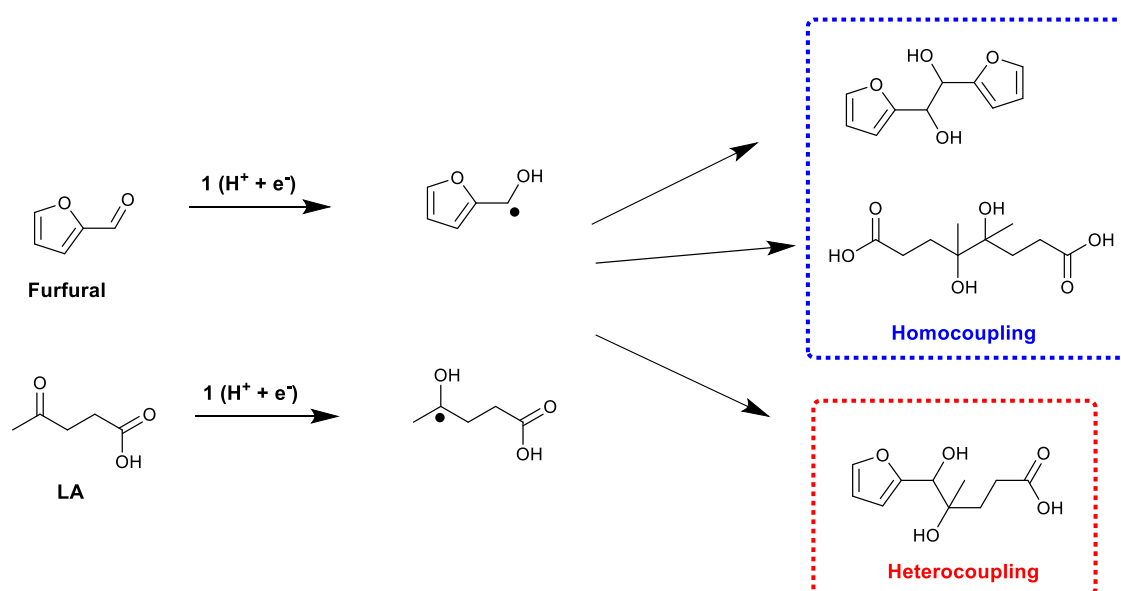


Figure 4.9.4. Electrochemical performance of MTAP catalysts for furfural reduction. LSVs were taken before (dashed line) and after (solid line) the addition of 8 mM furfural on (a) FeTAP, (b) NiTAP, (c) CoTAP, and (d) CrTAP. (e) Chronoamperometry of each catalyst and (f) Faradaic efficiencies of liquid products obtained after electrolysis at -0.50 V vs RHE. Reaction conditions: 0.1 M potassium bicarbonate-carbonate buffer (pH 10), 8 mM furfural, catalyst loading was 0.1 mg cm^{-2} . The scan rate for the LSVs was 50 mV s^{-1} and was scanned in the cathodic direction. All chronoamperometry experiments were held at -0.50 V vs RHE for one hour.

4.10 Can the Concept be Extended Towards Heterocoupling?

The results demonstrated in the previous section are an example of electrochemical C-C bond formation. In thermochemistry, C-C coupling is one of the most important reactions and is notoriously difficult as it entails the activation of unreactive C-H bonds using expensive Pd catalysts at high temperatures.²²⁶ During the electrochemical formation of hydrofuroin, C-C coupling was successful under mild aqueous conditions buffer at low overpotentials and room temperature. Insights into the mechanism revealed that the homocoupling of furfural most likely occurs via a radical coupling mechanism, after a PCET step to produce a radical species which couples in solution. An extension of this concept was attempted to try and couple furfural with LA to produce a novel cathodic heterocoupling reaction on single-atoms. An extra layer of complexity appears during heterocoupling reactions as it is difficult to control radical coupling once the species leaves the electrode surface, resulting in possible homocoupling between furfuryl radicals and LA radicals (**Scheme 4.10.1**).



Scheme 4.10.1. Electrochemical C-C bond formation between furfural and LA. Both homocoupling and heterocoupling between the radical species are possible.

CoTAP was chosen as the preferred candidate for the reaction as this material showed the highest activity and selectivity towards hydrofuroin. **Figure 4.10.1** shows the LSVs of CoTAP before and after adding 16 mM LA and then 8 mM furfural. A larger concentration of LA was used because straight-chain compounds tend to bind less intimately to electrode surfaces than aromatic compounds.¹³⁰ Furthermore, a 2:1 ratio of LA to furfural could decrease the rate of the homocoupling of furfural. Compared to the blank CoTAP sweep the onset potential moves slightly more anodic after the addition

of LA, suggesting LA reduction is taking place, and after furfural is added to the electrolyte, a slightly higher current was achieved suggesting both furfural and LA are being reduced under these conditions. For chronoamperometry measurements, a fixed potential of -0.50 V vs RHE was chosen as this was the potential at which the LA and furfural reduction sweeps seemed to overlap, possibly suggesting that both reductions were occurring simultaneously.

Due to the number of possible isomers available, NMR was not able to distinguish between hetero- and homocoupled products. Quantification after chronoamperometry measurements was instead attempted using liquid chromatography – mass spectrometry (LC-MS), however, the quantification process still needs to be optimised to be able to calculate FE and detect relevant products.

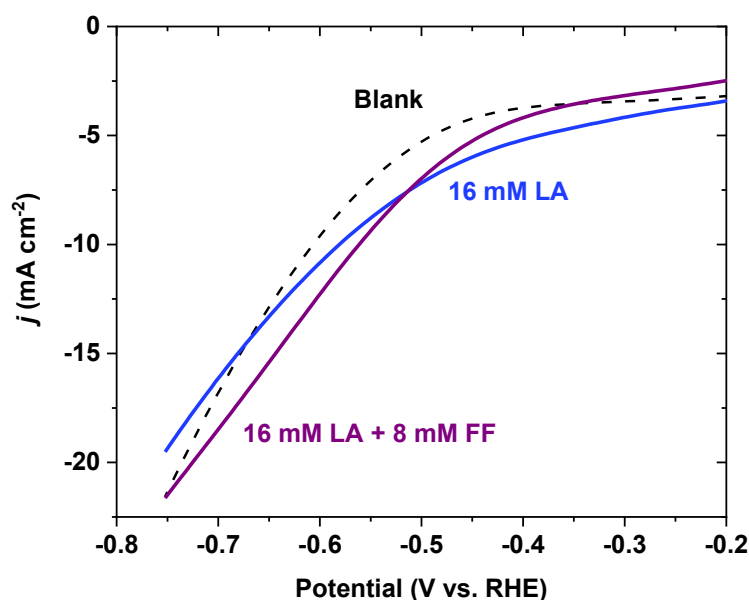


Figure 4.10.1. LSV of CoTAP cathodes for the heterocoupling between furfural and levulinic acid (LA). Reaction conditions: 0.1 M potassium bicarbonate-carbonate buffer (pH 10), CoTAP loading 0.40 mg cm^{-2} . The scan rate was 50 mV s^{-1} and was scanned in the cathodic direction.

4.11 Conclusion

In this chapter, successful investigations into the underlying furfural electroreduction mechanisms were undertaken. It was determined that selectivity towards FAL and 2-MF on Cu electrodes can be influenced, and that electroreduction activity was highly dependent on pH, with 2-MF selectivity requiring highly acidic pH for efficient production. Using a combination of DFT and experiments, more insights into the longstanding dispute in the literature regarding the mechanism of furfural reduction on Cu cathodes were found, which suggested that a PCET mechanism of reduction is preferred over an ECH route. Furthermore, the simulated reaction pathways suggested that different adsorbed intermediates are produced under different conditions, which could lead to different formed products.

Taking inspiration from the CO₂RR, CuPc and CoPc were tested for furfural reduction activity and were found to produce hydrofuroin, a precursor to drop-in jet fuels, in mild conditions. The weak binding energies between single-atom molecular catalysts and furfural steered selectivity towards hydrofuroin. A theoretical model which relates the binding energies of furfural and hydrogen with a variety of electrode materials was produced and concluded that weaker binding energies are more selective to produce hydrofuroin, with moderate and strong binding energies leading to FAL and 2-MF formation. This methodology of catalyst selection provided a top-down approach to aid in designing better catalysts for the future. Further experimental studies revealed that hydrofuroin production is a first-order reaction mechanism with the rate-determining step being the first PCET step to produce the furfuryl radical, which immediately dissociates from the electrode to couple in solution, also suggested by other studies using state-of-the-art Pb.¹⁰⁷ ToF-SIMS studies showed that CoPc was slightly more stable than CuPc under reducing conditions.

The concept was extended further towards the heterocoupling between LA and furfural. Electrochemical activity suggests that carbonyl reduction indeed takes place, however, quantification of heterocoupled products is still underway.

The top-down approach to producing new cathode materials was studied further to attempt to steer selectivity away from hydrofuroin on single-atom electrocatalysts. The tunability of single-atom catalysts was demonstrated by changing the nature of the central metal atom. DFT models predicted CrTAP would yield larger quantities of FAL on the basis that CrTAP binds stronger to hydrogen and furfural in comparison to other single-atom catalysts. Experiments confirmed these theoretical predictions whereby FAL was produced with 16.1% FE. There is now confidence that further modifications of these catalysts can produce a wider range of reduction products such as 2-MF, and the same concept can be used for other organic substrates other than furfural.

Appendix A

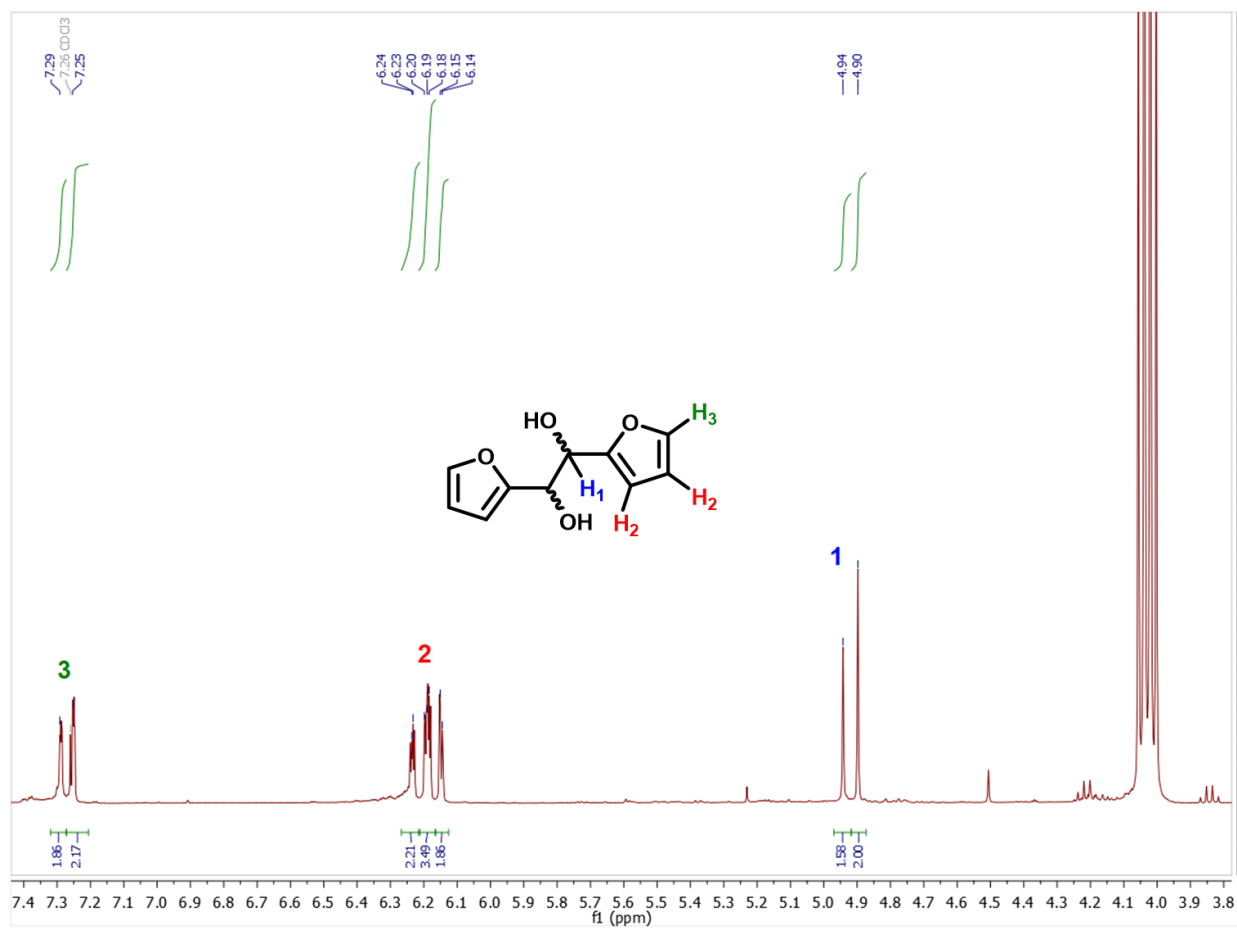


Figure A1. ^1H NMR (400 MHz, CDCl_3) spectra of hydrofuroin. The peak at around ~ 4.0 ppm is a result of ethyl acetate solvent.

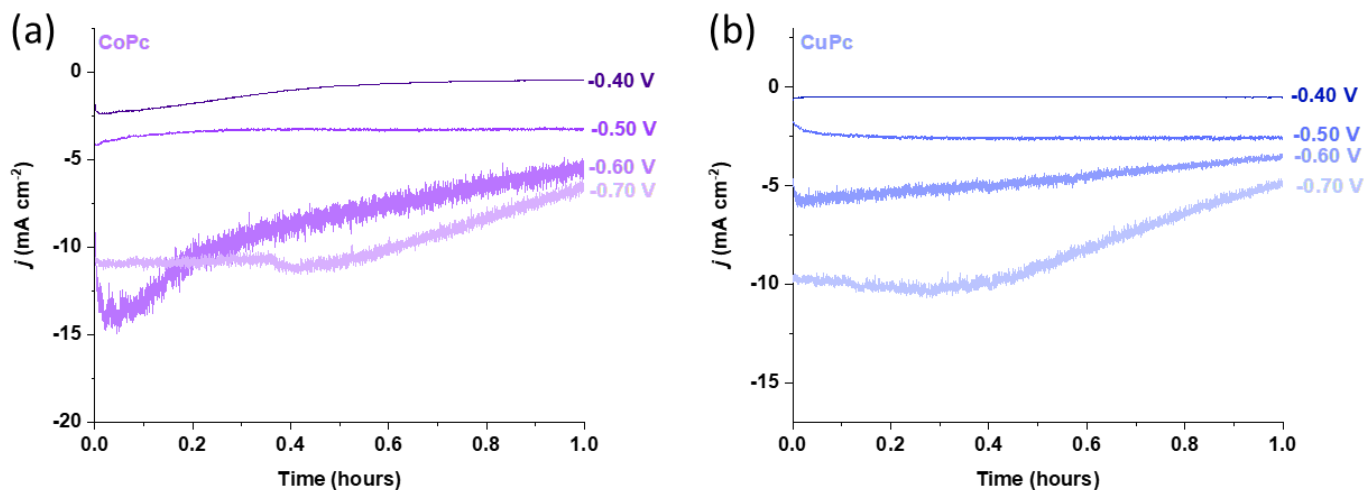


Figure A2. Chronoamperometry of (a) CoPc and (b) CuPc at varying potentials. Reaction conditions: 0.1 M potassium bicarbonate-carbonate buffer (pH 10), 8 mM furfural, potential applied for 1 hour, catalyst loading was 0.1 mg cm^{-2} .

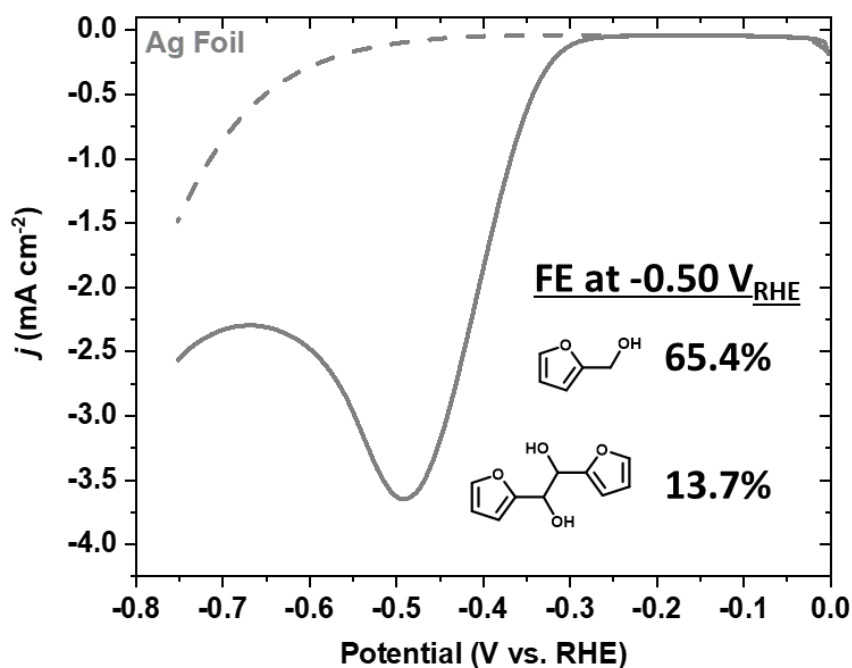


Figure A3. LSV of Ag foil before (dashed line) and after (solid line) the addition of 8 mM furfural. Reaction conditions: 0.1 M potassium bicarbonate-carbonate buffer (pH 10), 8 mM furfural, applied potential -0.50 V vs RHE for 3 h. The scan rate was 50 mV s^{-1} .

5 | Electrochemical Production of Amines

A manuscript for the content in this chapter has been produced and is ready to be submitted for peer-review. The results in this chapter were obtained by the author of this thesis with credit given to other contributors throughout the chapter. In brief, all DFT calculations were obtained by Sihang Liu, and Dr Soren B. Scott supervised me using the sputter deposition tool, Yuxiang Zhou obtained SEM, XPS, and EDX images in this chapter.

5.1 Objective and Motivation

Nitrogen-containing organic compounds are a very important class of chemicals which are used in medicines, polymers, and agrochemicals.²²⁷ However, the inherent incorporation of nitrogen moieties in biomass is limited, usually only appearing in amino acids, nucleic acids, and some polysaccharides like chitin.⁷¹ This chapter explores methods to electrochemically synthesise amines using external nitrogen sources, to produce furanic and aliphatic amines. By introducing nitrogen moieties into the platform chemicals HMF and furfural, a wider variety of high-value chemicals is available (**Figure 5.1.1**), some of which can be more valuable than standard oxidation/reduction products.

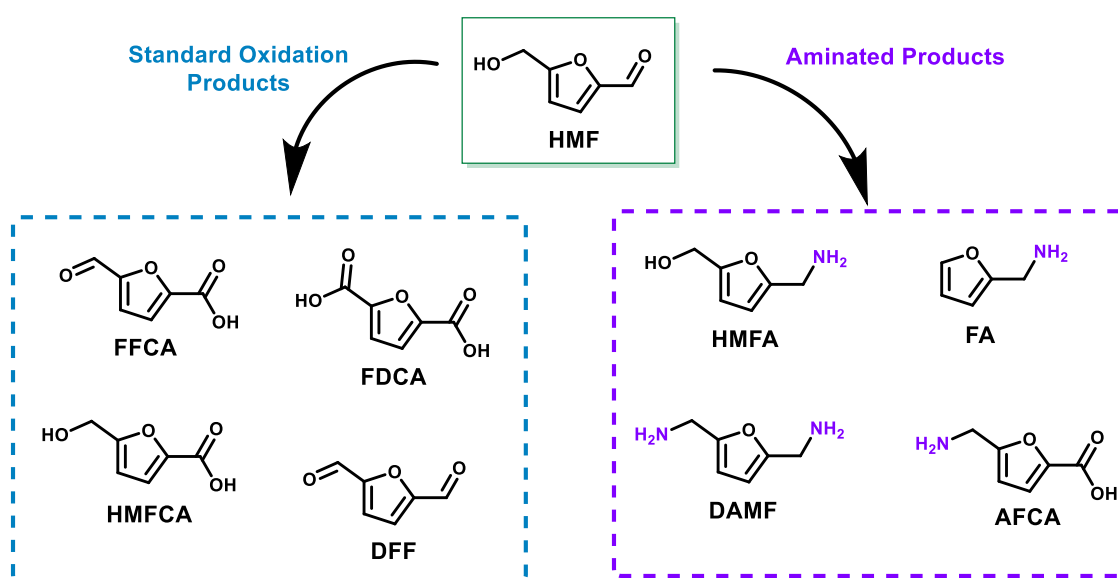


Figure 5.1.1. List of potential furanic compounds available from standard HMF oxidation compared to HMF amination. A more diverse set of compounds are available following amination.

Currently, in literature, aqueous electrochemical amine synthesis has a limited number of publications, and the underlying mechanisms are not very well explained. As specified in **section 2.3**, a report from Figueiredo highlighted that finding mechanisms of amination reactions can help with future developments in this field.¹⁶⁰ To help address this, a combination of DFT and experimental studies are used to determine possible electrode properties that are best for the electrochemical reductive amination of HMF. The effects of pH, electrode material, applied potential, and initial biomass concentration are all explored to optimise reaction parameters to produce HMFA as efficiently as possible.

The present industrial synthesis of important drugs usually requires more than one synthesis step,²²⁸ which in turn require intermediate species to be extracted and purified before each step. This can be

environmentally damaging due to the amount of organic solvents used during chromatographic purification. Through electrochemistry, the need for separating intermediates before individual reaction steps can be negated, due to the selectivity benefits that electrosynthesis provides. After producing HMFA via electrochemical reductive amination, efforts are made to selectively oxidise HMFA into AFCA in the same electrolyte. Attempts to produce a first-of-its-kind multistep electrochemical process to produce AFCA from HMF will be presented here, which involves firstly electrochemically reductive amination of the aldehyde group, then oxidation of the alcohol group without any purification between the steps (**Figure 5.1.2**).

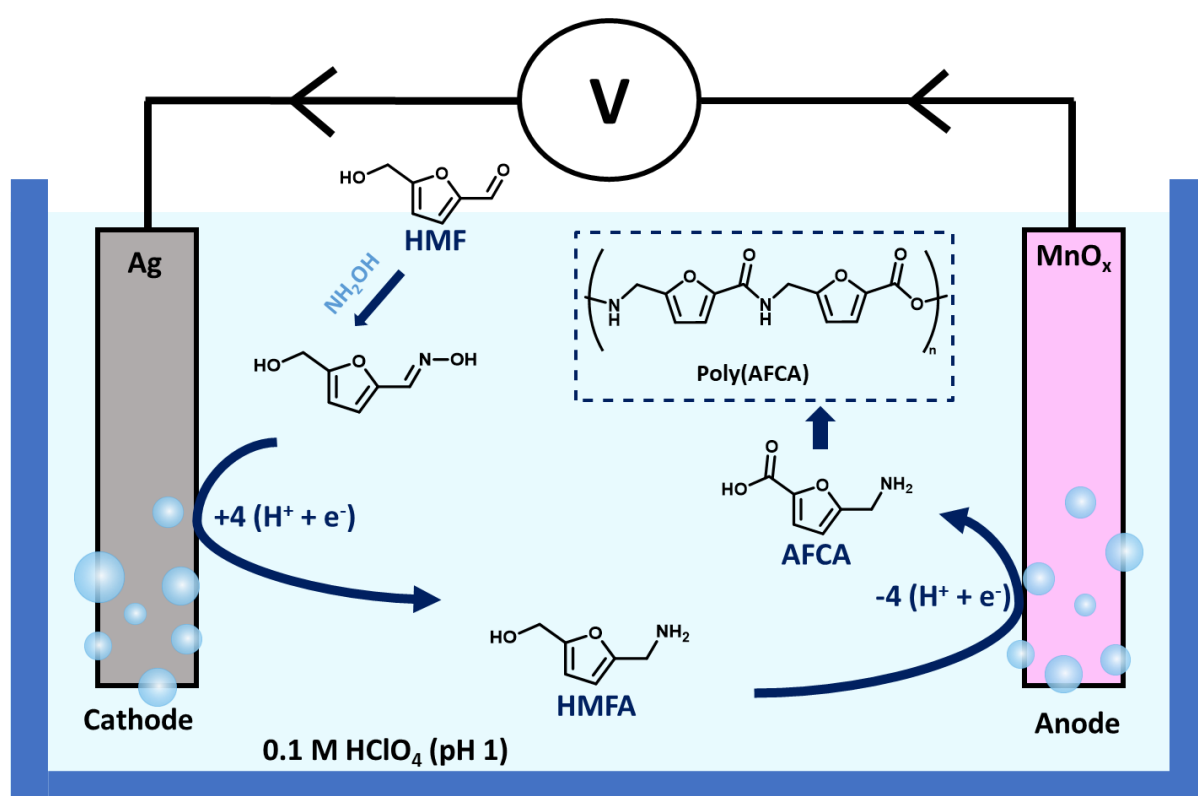


Figure 5.1.2. The two-step electrochemical production of AFCA from HMF and NH_2OH using Ag and MnO_x electrodes, as well as the possible polyamide possible from AFCA self-polymerisation.

An expansion of the concept is then extended to produce aliphatic amines. A new method to produce 1,2-diamines is explored using CoTAP single-atom catalysts that were used to couple furfural in Chapter 4. This process demonstrates the ability to produce useful diamines at a low operating potential of -0.50 V vs RHE and takes inspiration from our previous work on hydrofuroin production from furfural reduction.

Finally, we attempt to make the electrochemical reductive amination of HMF a continuous process by designing an MEA device, which consists of different forms of Ag cathode materials such as

nanoparticles and electrodeposited foams. This demonstrates a potential commercial scale-up for this process once the MEA system is optimised.

5.2 Finding Ideal External Sources of Nitrogen

The electrochemical reductive amination reaction is a powerful way of producing amines in mild aqueous conditions. The first step of this process involves the nucleophilic addition of a nitrogen-containing species to a carbonyl bond, eliminating water in the process (**Figure 5.2.1a**). This is a non-electrochemical process which occurs spontaneously in solution to form an equilibrium, which can be shifted towards the aminated intermediate species either by using a stronger nucleophile or by adding a high concentration of the nitrogen source. NH_3 was tested as a suitable green nitrogen source as research is underway to make the production of NH_3 an electrified process.²²⁹ NH_3 was added to 20 mM furfural solution which should result in an imine intermediate, however, NH_3 is a weak nucleophile and even a 6 M ammonia/ammonium sulphate buffer was unable to convert all the furfural into the imine (**Figure 5.2.1c**). Using such high concentrations of NH_3 comes with drawbacks as we are limited to alkaline pH for any electrochemical reactions, and some common electrodes used for electrochemical reduction reactions such as Cu, are dissolved in concentrated NH_3 solutions.²³⁰ NH_2OH , which is a product of NH_3 oxidation, was tested as an alternative nitrogen source. The lone pair of electrons on the OH group can be advantageous as it significantly increases the nitrogen nucleophilicity. In organic chemistry, nucleophilicity is measured using the Mayr scale, and the lone pair of the OH increases the nitrogen nucleophilicity through what is known as the alpha effect.²³¹ This effect pushes the Mayr scale nucleophilicity for NH_2OH to ~ 15 , compared to ~ 10 for that of NH_3 , so, in theory, would require less amounts of NH_2OH for a complete conversion of furfural into its oxime intermediate.

Figure 5.2.1b shows NMR spectra of 20 mM furfural reacting with different equivalents of NH_2OH . The spectra suggest that only a 1:1 equivalence of NH_2OH (20 mM of each) to furfural is required to convert almost all the initial furfural, in stark comparison to 6 M NH_3 barely managing to convert 50% of the added furfural into its imine.

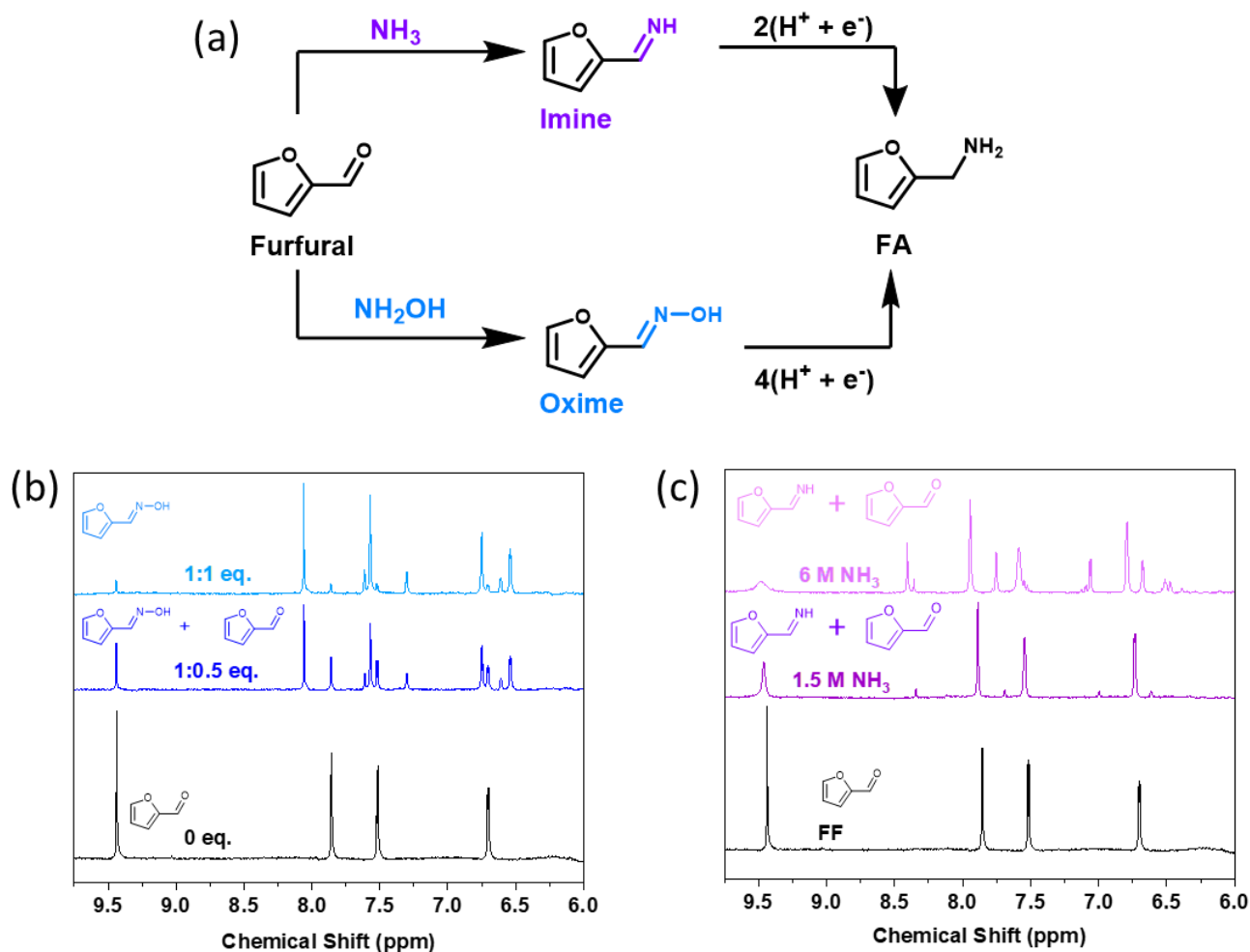
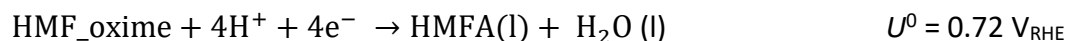
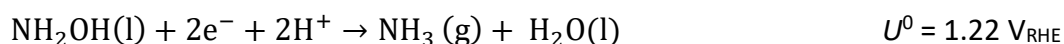


Figure 5.2.1. Nucleophilic addition of nitrogen sources to 20 mM furfural solution. (a) Scheme of electrochemical reductive amination of furfural using different external nitrogen sources. (b) Furfural and NH_2OH in different equivalents. Results are similar in both pH 1 and pH 10 solutions. (c) Furfural in different concentrations of ammonia/ammonium sulphate buffer.

An incomplete formation of the imine using NH_3 is detrimental to electrochemical reductive amination activity because it leaves behind furfural molecules which could be irreversibly reduced into FAL. In this regard, NH_2OH was chosen as the nitrogen source for all following reductive amination experiments as we were able to see a near 100% conversion in both pH 1 and pH 10, suggesting that the nucleophilic addition could be independent of pH, unlike NH_3 , which naturally requires alkaline pH. This gives the electrochemical reductive amination using NH_2OH a wider range of optimising parameters including pH, which was found to be a significant factor in electrochemical reduction reactions in Chapter 3; with a low pH usually preferred for this reaction.

5.3 Screening of Suitable Electrodes for Reductive Amination

The mechanism of electrochemical reductive amination of furfural can be considered an extension of furfural electroreduction as it draws some similarities of the reaction studied in the previous chapter. The main difference is that an oxime is first formed via nucleophilic addition, which will be the species that will adsorb onto the electrode to be reduced similarly to furfural reduction. Like furfural electroreduction, both reactions may include the same initial first step of the Volmer reaction, and hence the HER must be suppressed to achieve a high Faradaic efficiency for the reductive amination. An extra layer of complexity is present during the electrochemical reductive amination reaction if NH_2OH is used as the nitrogen source, due to the electrochemical reduction of NH_2OH into NH_3 and H_2O also being a competing reaction. To minimise the rate of NH_2OH reduction, only a 1 to 1 equivalent of NH_2OH to carbonyl bonds was used in all experiments in this chapter, with the assumption that none of the NH_2OH will be left in solution after complete addition onto the furanic species, leaving only HER as the main competing reaction. The reactions which are involved in this process are denoted below along with their calculated equilibrium potentials.



The activity of various metal surfaces for HMF reductive amination in acidic electrolytes was studied, as disubstituted furanic compounds can yield a wider range of valuable amines. A low pH was chosen for this reaction to increase the rate of hydrogen adsorption, as well as protonating the oxime intermediate species to improve the rate of biomass adsorption to the cathode. The electrodes tested included Ag, Pt, Cu, Sn, Au, and Pb, in a 0.1 M HClO_4 solution (pH 1) using 10 mM HMF and NH_2OH . For each test, the LSV in **Figure 5.3.1** shows a blank sweep of the electrolyte being taken, followed by a sweep after 10 mM NH_2OH addition, then a final sweep after 10 mM HMF addition and leaving the mixture to stir for 10 minutes to react all the NH_2OH with the carbonyl groups. The increase in current density for the blank sweep is attributed to the HER, the increase in current after adding NH_2OH , to NH_2OH reduction, and similarly to the electrochemical reduction of the HMF-oxime intermediate after adding HMF to the electrolyte. For the reductive amination under these conditions, we observed that Ag and Pb electrodes displayed an onset potential (defined here as the potential needed to achieve -1 mA cm^{-2}) which is much more anodic compared to the HER or NH_2OH reduction, and on Ag, a mass transport limitation is even reached suggesting Ag is very active at reducing the HMF-oxime into

HMFA, with HER likely dominating after -0.80 V vs RHE. A similar pattern was seen on Cu and Sn electrodes, but with a much smaller window before the relative onsets of the HER and NH_2OH reduction. Furthermore, Sn electrodes required a more cathodic potential for HMF-oxime reduction compared to Ag, Pb and Cu surfaces. The LSVs of Pt and Au electrodes suggested that both competing reactions have onset potentials that are slightly more anodic than biomass reduction, concluding that these cathodes are not suitable for the reductive amination reaction due to too much competition with side reactions, lowering Faradaic efficiency.

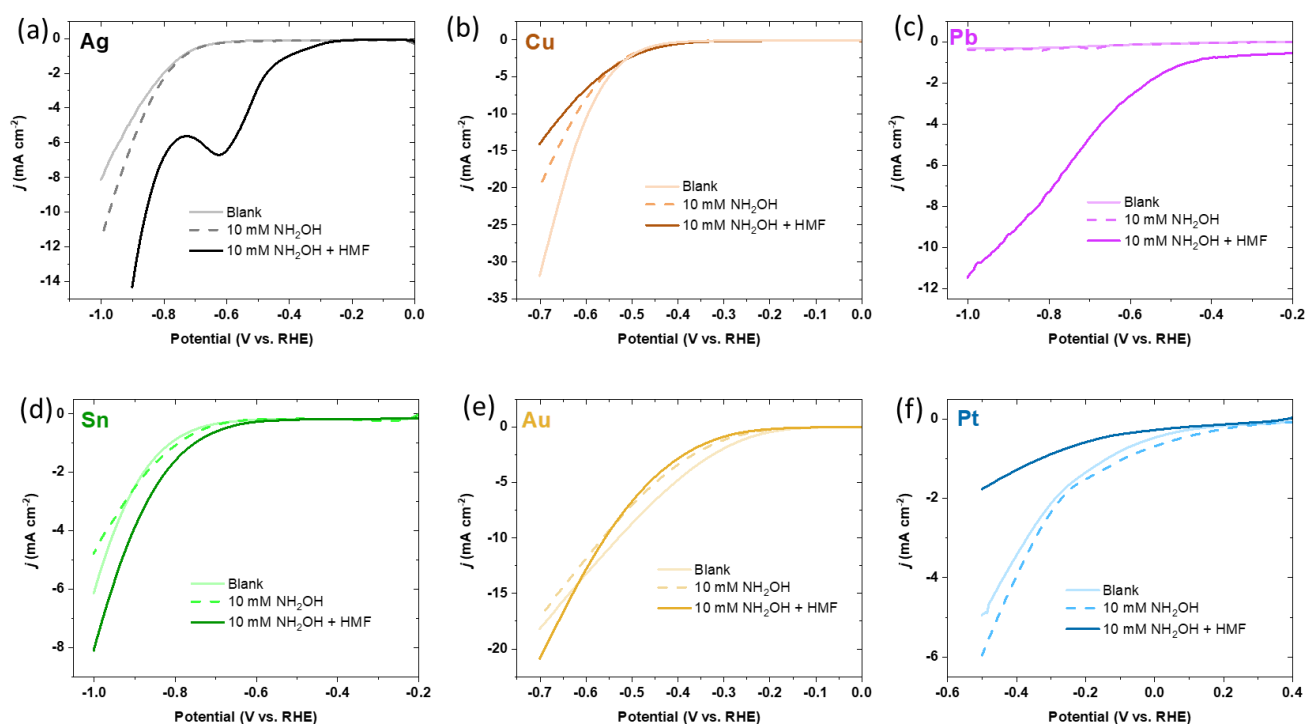


Figure 5.3.1. Linear sweep voltammograms of potential electrode materials for electrochemical HMF amination on (a) Ag, (b) Cu, (c) Pb, (d) Sn, (e) Au, (f) Pt. Reaction conditions: 0.1 M HClO_4 electrolyte (pH 1), 10 mM HMF added to 10 mM NH_2OH . The scan rate was 50 mV s^{-1} and was scanned in the cathodic direction.

Ag electrodes were chosen as the primary focus of further optimisation due to their apparent superior reductive amination activity, which has advantages over Pb including fewer toxicity issues, and greater current density at around -0.50 V vs RHE. We also note that Pb electrodes have a notoriously high overpotential for the HER. Whilst this may seem beneficial for lowering HER rates, the adsorption of hydrogens on the electrode surface can be a possible route for the HMF-oxime reduction, similar to 2-MF production during furfural reduction on Cu. We believe Ag electrodes may provide an ideal balance for both reactions leading to a higher efficiency of amine formation.

5.4 Why is Ag so Good?

To help unravel the origin of the high activity of Ag electrodes for the electrochemical reductive amination, our collaborators conducted DFT studies to produce a free energy diagram showing the individual steps required for the electrochemical production of HMFA from HMF and NH_2OH at 0 V vs RHE. The addition of NH_2OH onto the carbonyl bond of HMF was very exothermic and could explain why only a 1:1 equivalent was needed for near 100% yield of the oxime. Three possible routes to produce HMFA are possible on the modelled Ag(111) surface, with the most exothermic route (**Figure 5.4.1** green route) being seen as the most feasible route. Here, there is only one slightly endothermic reaction, $\text{CHNH}^* \rightarrow \text{CHNH}_2^*$, as opposed to the other routes which have endothermic steps and could hence be potential dependent. We see that the most feasible step goes through a deoxygenation step to remove the OH group before any C-N bond cleavage, which may suggest that pH has a big role in overall efficiency. It is possible that a low pH may protonate this OH group into $^+\text{OH}_2$ which is a more stable leaving group.

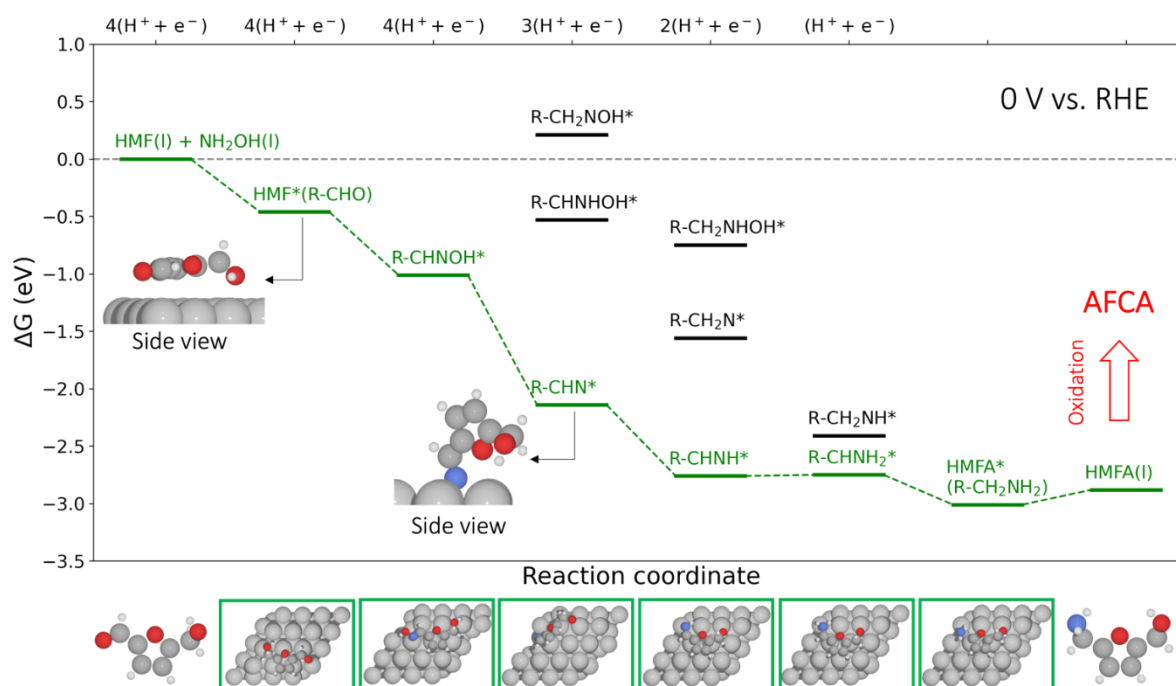


Figure 5.4.1. Free energy diagram of calculated energies to produce HMFA from HMF using NH_2OH as the nitrogen source, on an Ag(111) surface at 0 V vs RHE. DFT simulation was done by Sihang Liu.

5.5 What Other Parameters Affect Amination Activity?

5.5.1 Effect of pH

An advantage of using NH_2OH as the nitrogen source is the ability to have pH as a variable parameter because nucleophilic addition of NH_2OH across a carbonyl bond appeared to be independent of pH. Following this, the pH of the electrolyte was studied for its effect on the rate of electrochemical reductive amination of HMF. When using NH_2OH as the nitrogen source, a high pH ($>\text{pH } 13$) is detrimental to the stability of both HMF and the resultant HMF-oxime and could result in the formation of nitro-containing by-products.²³² Usually, a multi-step electrosynthesis process such as the production of AFCA from HMF, requires an amination followed by an OH oxidation, and it could be possible that both reactions favour a different pH. Therefore, an electrolyte which can accommodate both reactions would be ideal, as all that is needed is an electrode change opposed to a reagent-heavy pH shift between each step. We attempted to see if any electrodes could be used to aminate HMF in a mildly alkaline pH 10 bicarbonate-carbonate buffer electrolyte, as we show that HMF does not rapidly degrade at this pH in a later chapter in this thesis. **Figure 5.5.1.1** shows LSVs of HMF amination using Ag, Pt, Au, and Pb in pH 10. Again, we see that Ag and Pb electrodes show some activity for HMF-oxime reduction. However, the onset potential on Ag is much closer to the supposed HER and NH_2OH reduction compared to pH 1 electrolytes. This may have compromised selectivity due to competition with side reactions. Ag and Pb electrodes were able to produce very small amounts of HMFA at -0.50 V vs RHE ($<10\%$ FE), with the missing FE likely due to HER or the formation of side products occurring from ring opening and other reactions. Hence, we concluded that an acidic pH is necessary for amination using NH_2OH . This is probably because the oxime needs to be protonated to better adsorb to the electrode, along with increased H^+ on the electrode surface for HMF-oxime reduction.

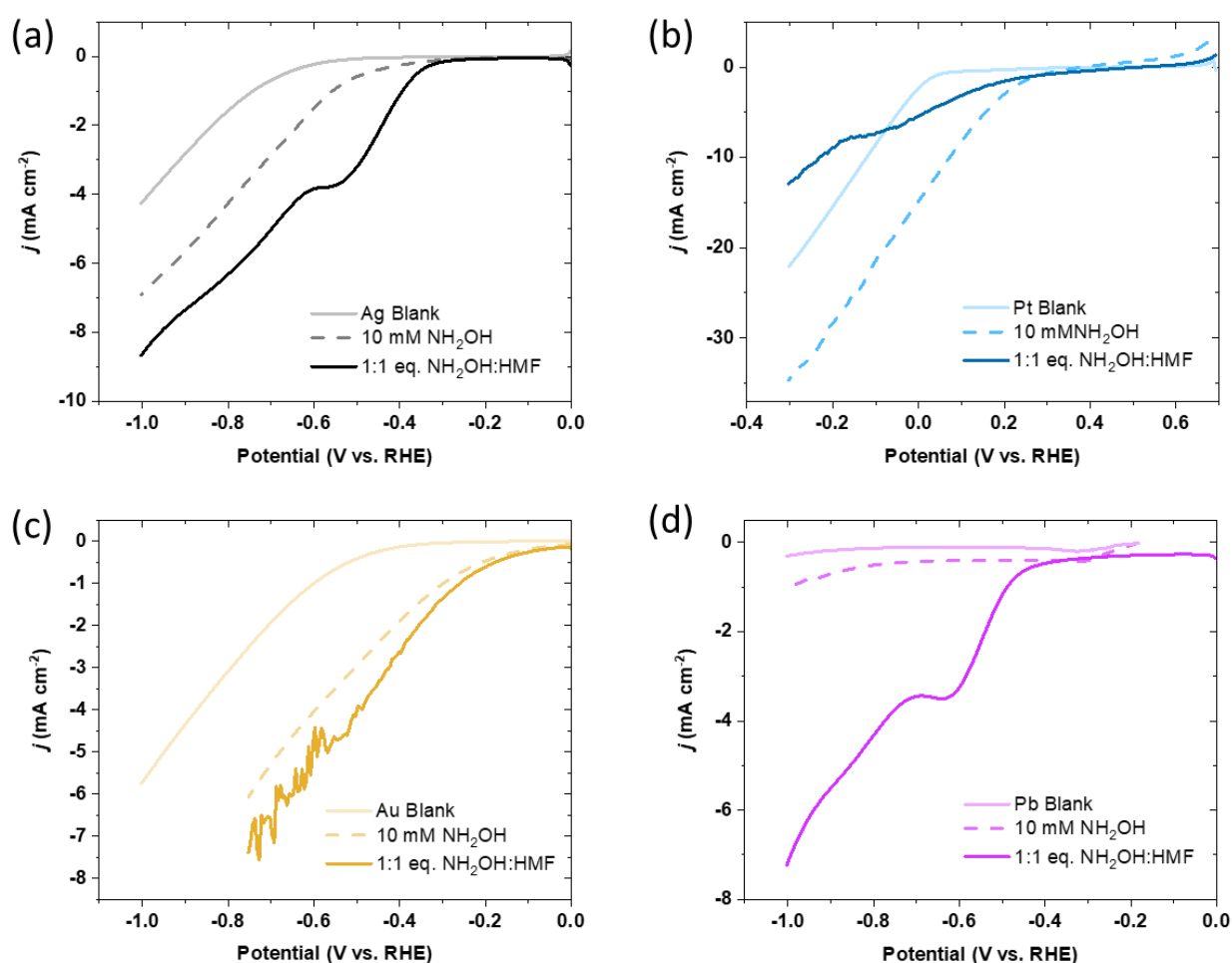


Figure 5.5.1.1. Screening of potential electrode materials for HMF reductive amination on (a) Ag, (b) Pt, (c) Au and (d) Pb surfaces in a pH 10 electrolyte. Reaction conditions: 0.1 M potassium bicarbonate-carbonate buffer (pH 10), 10 mM NH_2OH added to 10 mM HMF. The scan rate was 50 mV s^{-1} and was scanned in the cathodic direction.

To explore the effect of pH further, varying acidic pH solutions were studied containing 10 mM HMF and NH_2OH with the LSVs, FEs, and partial current densities depicted in **Figure 5.5.1.2**. We see that the amination is most efficient at pH 1, and noticeably decreases when the pH is either lowered or increased. It seems that a pH closer to that of the pK_a of the oxime (~ 1.3) is an ideal value for this reaction and the significance of pK_a was seen in the works of Kwon et al.²³³ At pH 0.5, the onset of biomass reduction is almost at 0 V vs RHE. However, there is lower reductive amination FE in pH 0.5 compared to pH 1 at -0.50 V vs RHE, which is likely due to greater rates of HER. On the other hand, higher pH tends to lower the rate of oxime protonation which is likely the active species for reductive amination. Lower pHs will produce more of the active protonated oximes species which adsorb onto the electrode thereby increasing reductive amination activity, which is evident in the LSVs as the mass

transport limitation curves move slightly more anodic and displays a higher current at lower pH. There is a very low current density at pH 2, and we can conclude that pH 1 is the best pH for this reaction with the highest partial current density for the reductive amination reaction being recorded at this pH. Hence, this pH was chosen for further optimisation reactions. Whilst the chosen potential for all these experiments was -0.50 V vs RHE, it is likely that the maximum partial current density for HMF amination may be obtained at different potentials depending on the rate of the competing HER.

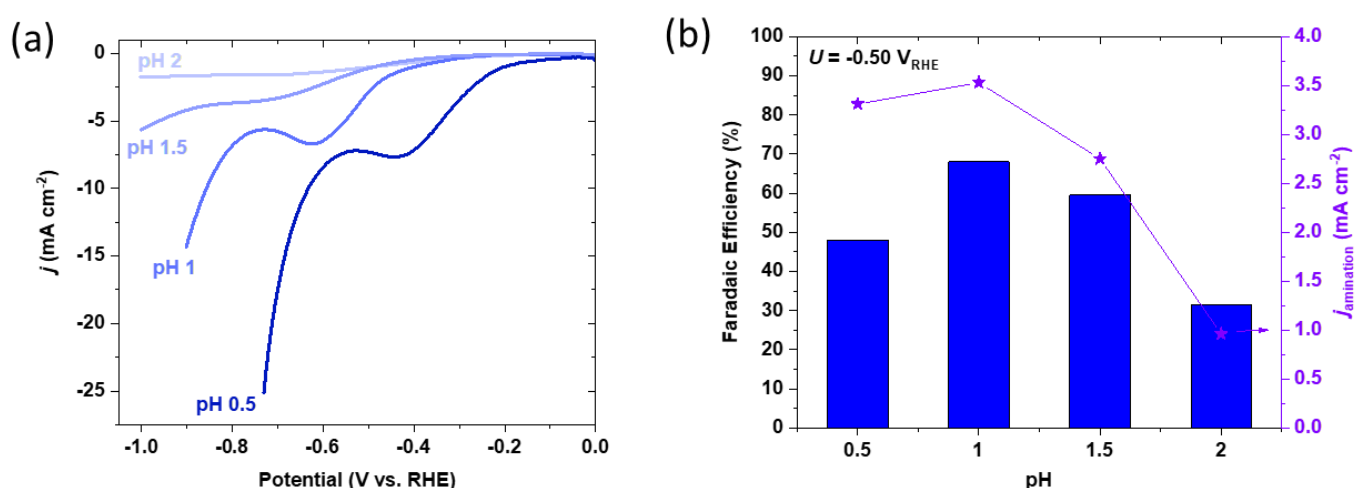


Figure 5.5.1.2. Study of the effect of pH on HMF reductive amination. (a) LSVs of 10 mM HMF and NH₂OH at different acidic pH. (b) Blue bars graph representing Faradaic efficiencies of HMFA production at varying acidic pH. Purple lines depicting the calculated partial current densities of the amination reaction. Reaction conditions: 0.1 M HClO₄ electrolyte, the applied potential was -0.50 V vs RHE for 3.5 hours. The scan rate was 50 mV s⁻¹ and was scanned in the cathodic direction.

5.5.2 Effect of Initial Biomass Concentration

To maximise reductive amination rates, normally a high concentration of initial biomass feedstock is preferable. However, due to the instability of HMF at high concentrations, the optimal initial starting concentration must be carefully decided. Too high concentrations of HMF and NH_2OH may result in the formation of humin side products which will affect selectivity because furanic aldehydes react with each other in high concentrations to produce humins,²³⁴ which can poison the electrode surface negatively affecting the FE.

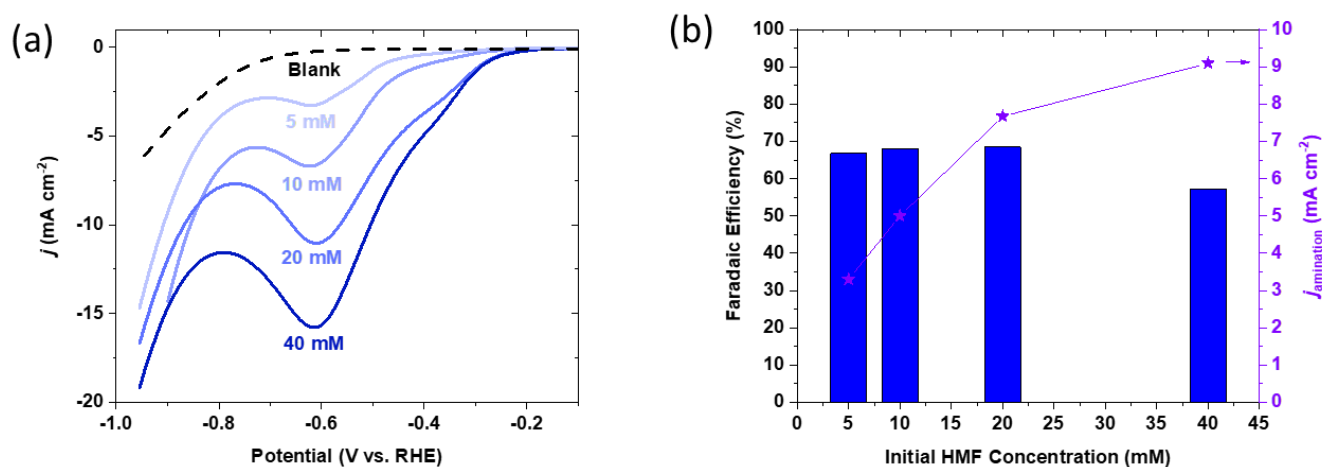


Figure 5.5.2.1. Study of the effect of initial HMF+ NH_2OH concentration on the efficiency of reductive amination on Ag foil. (a) LSVs of differing initial concentrations of HMF and NH_2OH in 1:1 equivalents on Ag electrodes. (b) Blue bars represent the Faradaic efficiency of HMFA production after constant potential experiments. Purple line depicting the partial current densities of the reductive amination reaction. Reaction conditions: 0.1 M HClO_4 electrolyte, applied potential for each experiment was -0.50 V vs RHE for 3.5 hours. The scan rate was 50 mV s^{-1} and was scanned in the cathodic direction.

On the H-cell setup, the optimal concentration on 1 x 1 cm² Ag foil was investigated. **Figure 5.5.2.1a** shows LSVs and the FE of HMFA obtained by varying initial HMF and NH_2OH concentration, and as expected, the current densities increase with greater amounts of the HMF-oxime in the electrolyte. The FE of the amination remains mostly constant around ~65% for low concentrations (5-20 mM HMF), with an almost linear increase in partial current density under these conditions (**Figure 5.5.2.1b**). The FE decreases at 40 mM of starting biomass, which is probably due to side product formation and electrode poisoning, as a noticeable organic film was seen on the electrode surface. The partial current density also begins to decrease with increasing concentration suggesting the reaction efficiency has been decreased likely due to a combination of electrode poisoning and HMF degradation. As a 1 x 1 cm² of Ag foil was used, it is possible to conclude that 20 mM of HMF and NH_2OH is the optimal concentration per cm² of Ag foil. This can be increased further through methods

of increasing the surface area of Ag could be increased by using Ag nanoparticles or foam to increase current densities further.

5.6 Reductive Amination of Other Furanic Feedstock

The two substituent groups at the 2 and 5 positions on HMF can yield other carbonyl products because HMF has two reactive functional groups (CHO and CH₂OH), meaning that other carbonyl products are possible, which can be aminated. These include DFF, FFCA and furfural (after HMF decarboxylation). Electrodes exist which can selectively form these products such as Pt being reported to produce DFF.⁶ The partially oxidised furanic compounds were studied to see if they can be aminated to yield a wider variety of amines. These include furfurylamine (FA), 5-(aminomethyl)furan-2-carboxylic acid (AFCA), and 2,5-bis(aminomethyl)furan (DAMF), which are very useful compounds used in polyamides and pharmaceuticals.²³⁵

Figure 5.6.1a shows LSVs in electrolytes containing 10 mM of each of these intermediates in pH 1 and their corresponding aminated products detected on Ag electrodes at -0.50 V vs RHE. All these compounds show good FE towards amination with DFF amination being the least efficient. DFF contains two aldehyde groups so a 2:1 equivalence of NH₂OH (20 mM) to DFF (10 mM) was used. A far greater current density was reached during DFF amination compared to the mono-carbonyl species, likely due to more of the active protonated oxime species present which leads to an increase in reductive amination activity. A slight decrease in FE is not surprising here as partially aminated products could be present, as well as a greater likelihood of substrate degradation for the dioxime intermediate. DAMF is a useful compound as it can be coupled with dicarboxylic acids such as FDCA, to form a polyamide with a similar structure to that of Kevlar, the difference being the benzene ring being replaced with a furan. In addition, AFCA is also very useful as it is an amino acid which can be produced entirely electrochemically. These results show promise that a wide variety of compounds can be electrochemically aminated which contain carbonyl groups.

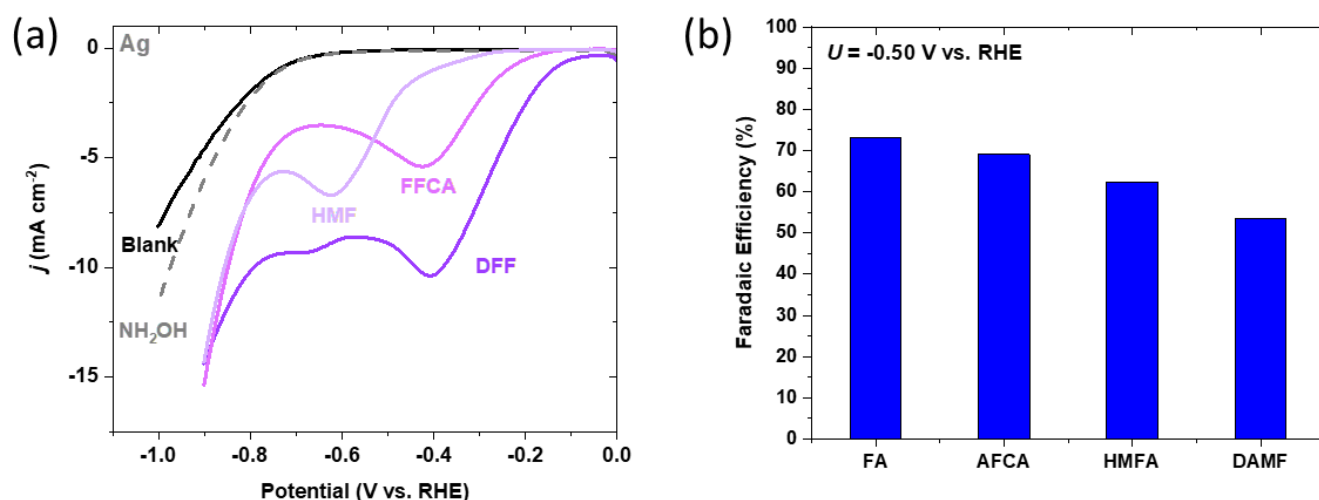


Figure 5.6.1. Electrochemical reductive amination of biobased carbonyl compounds on Ag electrodes. (a) LSVs of Ag electrodes before and after the addition of 10 mM DFF, HMF and FFCA. The amount of NH₂OH added was a 1:1 equivalent for HMF, furfural, FFCA, and 2:1 equivalent for DFF. (b) Faradaic efficiencies of the produced aminated products from different starting materials. Reaction conditions: 0.1 M HClO₄ electrolyte, the applied potential was -0.50 V vs RHE for 3.5 hours. The scan rate was 50 mV s⁻¹ and was scanned in the cathodic direction.

5.7 A New Multistep Electrosynthesis Process

Most industrial chemical syntheses involve more than one chemical conversion step. In thermochemistry, separation and purifications are required before each step which uses large amounts of organic solvents. In electrochemistry, it can be possible to avoid this separation by simply changing the electrode material and applying a specific potential that is selective in converting a specific functional group. In this regard, after producing HMFA using reductive amination, the CH₂OH group of HMFA can undergo further oxidation to selectively convert the CH₂OH group into a COOH group without affecting the amine, resulting in the biobased amino acid, AFCA. This molecule can then be self-polymerised to produce a fully renewable polyamide sourced directly from biomass. Ni foam electrodes have been reported to be efficient for electrochemical alcohol oxidation in alkaline media with good FE,¹³³ so were tested for HMFA oxidation into AFCA. A pH 13 KOH electrolyte was used for this conversion and the LSVs are depicted in **Figure 5.7.1a**. A blank sweep was taken, followed by a sweep after the addition of 10 mM HMFA which showed an oxidation wave at about 1.50 V vs RHE, which was not present in the blank sample, attributed to alcohol oxidation as it is unlikely that the amino group would be susceptible to oxidation under these conditions. After constant potential experiments at 1.60 V vs RHE, AFCA was detected with high FE (70%) using NMR, with chemical shift values matching literature values.^{236,237} Once combined with the reductive amination of HMF, we now present a multi-step, fully electrolysed process of producing this biobased amino acid for use in the polymer industry.

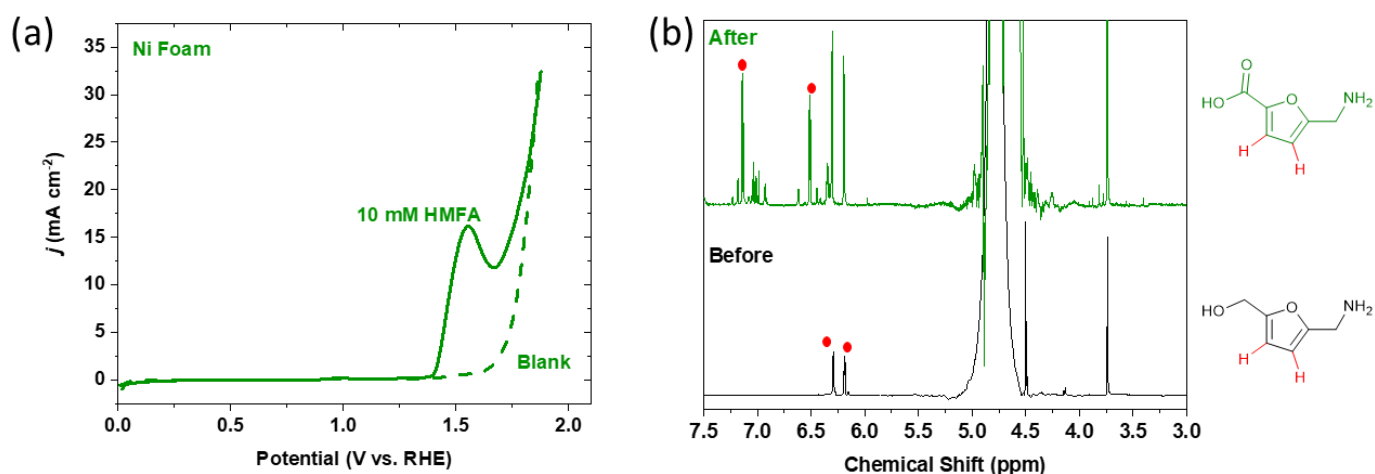


Figure 5.7.1. Electrochemical oxidation of HMFA to AFCA using Ni foam electrodes. (a) LSV of Ni foam before and after the addition of 10 mM HMFA. (b) ¹H NMR spectra of the electrolyte before and after chronoamperometry at 1.60 V vs RHE. Identifiable protons are highlighted with red dots and were compared to literature values^{236,237} to confirm that AFCA was produced. Reaction conditions: 0.1 M KOH electrolyte (pH 13), potential applied was 1.60 V vs RHE for 3.5 hours. The scan rate was 50 mV s⁻¹ and was scanned in the anodic direction.

Whilst Ni foam is suitable for HMFA oxidation, the two-step procedure to produce AFCA from HMF using Ni foam and Ag electrodes requires different pH solutions, which require a pH shift between the two processes. Whilst not too problematic, it would be preferable to not have a pH shift to lower the amounts of reagents needed for the reaction. For this, either the amination reaction needs to be feasible in pH 13, or the oxidation reaction needs to be feasible in pH 1 electrolyte. It has already been demonstrated that the electrochemical reductive amination reaction is difficult in alkaline media as it is difficult to produce the preferred protonated oximes at high pH, so the alcohol oxidation reaction in acidic media was focused on instead. Following this, MnO_x electrodes were produced via sputter deposition onto carbon paper electrodes to oxidise the alcohol group in HMFA into a carboxylic acid as previous studies have shown they can oxidise alcohols in pH 1.¹³⁷ The oxidation state(s) of Mn was difficult to identify using XPS (**Figure 5.7.2d**) so are labelled as MnO_x, although a significant proportion of Mn⁴⁺ was detected. **Figure 5.7.2a** shows LSVs of MnO_x before and after the addition of HMFA. Once again, an increase in current is seen relative to the blank sweep like that of Ni foam, which is again attributed purely to alcohol oxidation. After constant potential measurements at 1.60 V vs RHE, AFCA was detected with about 35% FE, alongside minor amounts of partially oxidised products. Compared to Ni foam in pH 13 however, MnO_x was much less active and selective. In addition, a greater number of unidentified products was seen using MnO_x electrodes, with over 50% of supplied electrons unaccounted for, likely from side oxidation reactions and catalyst degradation under these conditions. This is not too much of a surprise as MnO_x is known to be relatively unstable in acid, and can display

significant dissolution activity under these conditions,²³⁸ with our EDX imaging showing a reduction in Mn content after constant potential experiments further supporting this conclusion. From these results, we conclude that the MnO_x electrodes produced for these experiments are not feasible to use on a large scale in their current state unless methods to stabilise the MnO_x electrodes are found. Instead, it is likely that a pH shift and electrode switch to Ni foam after the reductive amination will need to happen if we wish to produce AFCA from HMF industrially.

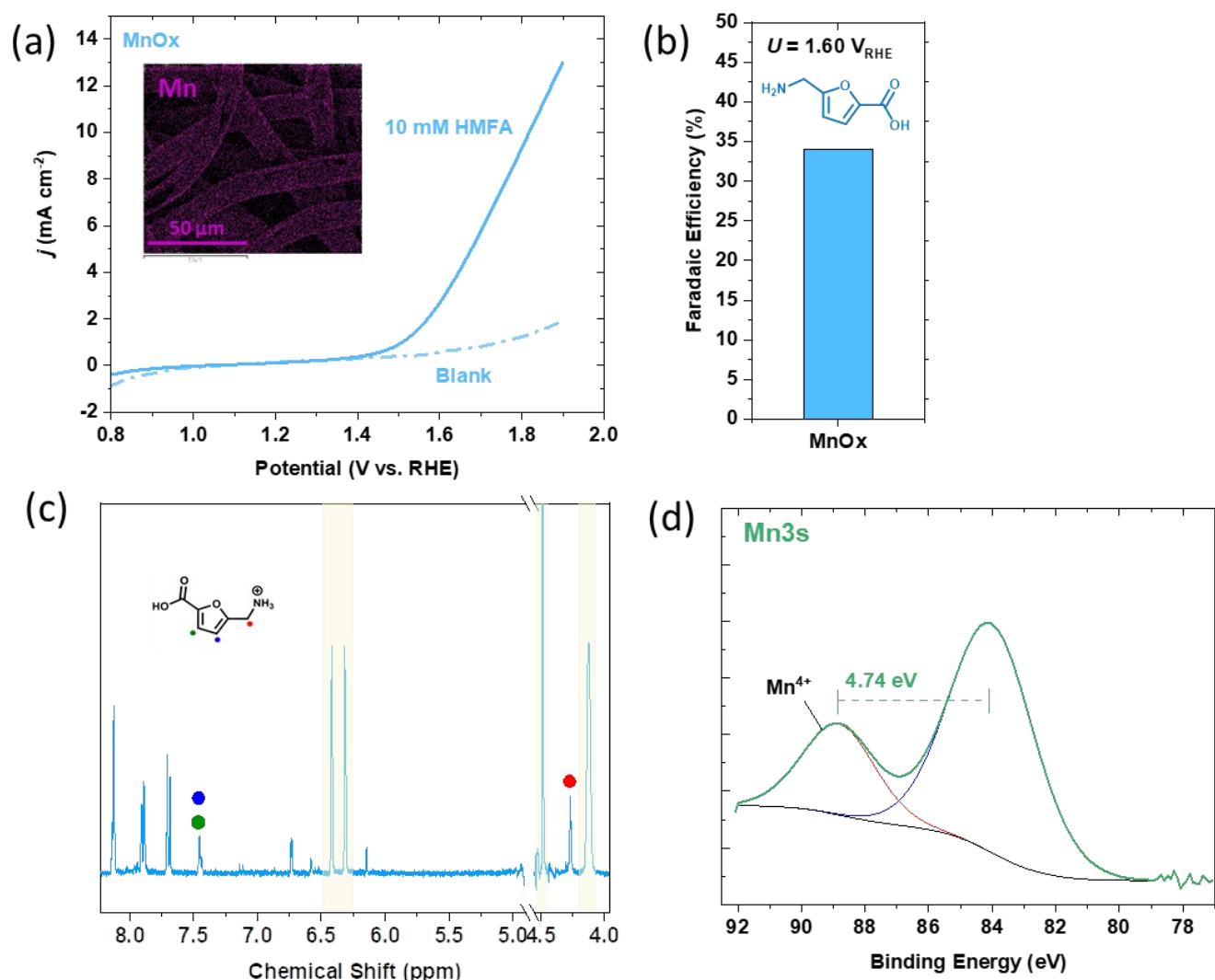


Figure 5.7.2. Electrochemical oxidation of HMFA in acidic electrolyte using MnO_x. (a) LSV of MnO_x electrodes before and after the addition of 10 mM HMFA. Inset of MnO_x EDX image before chronoamperometry. (b) Faradaic efficiencies comparing the detected reductive amination products using MnO_x electrodes. (c) ¹H NMR spectra post HMFA electrolysis on MnO_x electrodes. Highlighted regions represent peaks from HMFA starting substrate. (d) Mn3s core level XPS spectra of MnO_x electrode before chronoamperometry. Reaction conditions: 0.1 M HClO₄ (pH 1), the applied potential was 1.60 V vs RHE for 3.5 hours. The scan rate was 50 mV s⁻¹ and was scanned in the anodic direction. EDX image was taken by Yuxiang Zhou.

5.8 Continuous Electrochemical Reductive Amination

After initial optimisation in the H-cell, a potential scale-up of the reductive amination of HMF was investigated. **Figure 5.8.1c** shows the structure of the two-electrode flow cell which was designed and built, in an MEA configuration with the electrodes separated with a NafionTM membrane. An MEA configuration was chosen to minimise mass transport limitations. Ag materials were used as the cathode, with IrO_x and carbon being explored for the counter anode. For the cathode, different Ag materials were explored to increase the surface area by using commercial Ag nanoparticles (AgNPs), and electrodeposited Ag foam (**Figure 5.8.1b**) to increase current densities. Commercial IrO_x particles were used as the counter electrode as they are currently the best-reported catalyst for the counter-reaction of the OER, however, carbon paper was also tested as the counter electrode as a control.

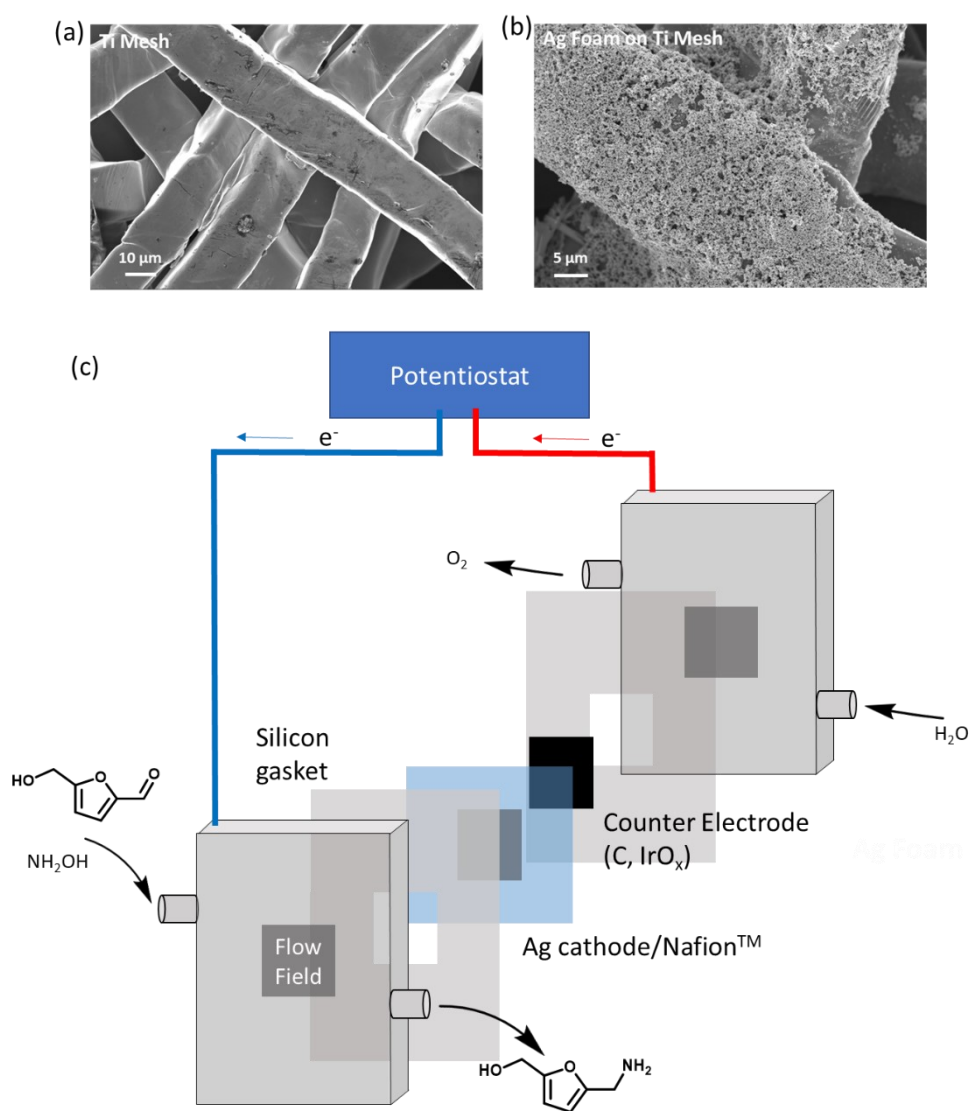


Figure 5.8.1. Continuous electrochemical reductive amination of HMF. SEM images of Ti mesh (a) and (b) Ag foam electrodeposited onto Ti mesh. (c) The designed two-electrode MEA system for the continuous electrochemical reduction of HMF to HMFA.

Figure 5.8.2a shows the LSVs of 2 mg cm^{-2} AgNPs before and after the addition of 40 mM furfural and NH_2OH , accompanied by the chronoamperometry of carbon paper and IrO_x counter electrodes. At -3.40 V, a greater current was observed using IrO_x as the counter electrode due to the greater efficiency of OER on IrO_x compared to carbon paper. NMR was used to detect HMFA in the electrolyte of both experiments and HMFA was formed on both systems, with a greater FE of $\sim 40\%$ using carbon paper electrodes compared to the 27% using IrO_x . Whilst the carbon paper may have a slightly higher efficiency, using the IrO_x counter had a greater activity, and produced a greater amount of HMFA after 3 hours.

Ag foam was electrodeposited onto a porous Ti mesh using the methods described in Chapter 3. The foam was also tested as a potential cathode material due to a theoretically greater surface area available for reduction capability. A successful synthesis was seen, and SEM images are displayed in **Figure 5.8.1a & b**. Surprisingly, the reduction activity of the Ag foam electrodes was much lower compared to the commercial AgNPs, most likely due to more surfaces being present for the HER to take place. We believe this process has promise but requires further optimisation. In the context of an industrial scale-up, AgNPs will likely be the most advantageous due to the ease of purchasing commercial Ag particles over electrochemically depositing Ag foam on Ti substrate.

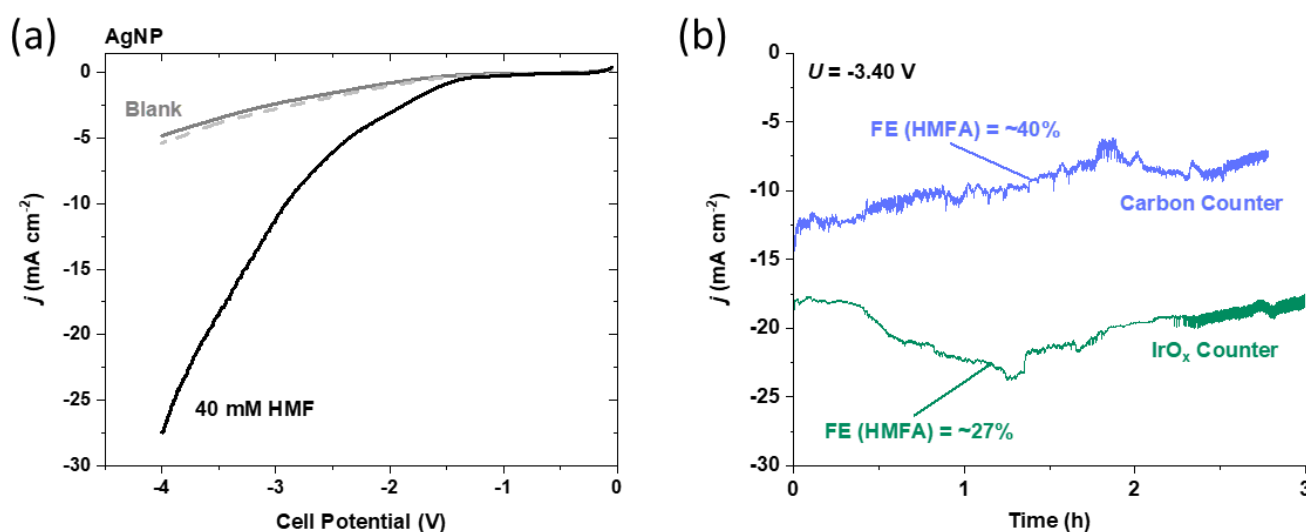


Figure 5.8.2. Continuous electrochemical reductive amination of HMF using AgNPs in a two-electrode MEA. (a) LSVs of AgNPs before and after the addition of 40 mM NH_2OH and HMF. (b) Chronoamperometry and reported Faradaic efficiency of HMFA production using different counter electrodes. Reaction conditions: 0.1 M HClO_4 electrolyte (pH 1), the applied potential was -3.40 V for 3 h, and AgNP loading was 2 mg cm^{-2} . The scan rate was 50 mV s^{-1} and was scanned in the cathodic direction.

Subsequent continuous HMFA oxidation in the two-electrode MEA was attempted using the sputtered MnO_x as the anode, with a Pt mesh cathode. The LSVs show an increase in current density after the addition of 30 mM HMFA, and constant potential experiments were done at 1.835 V. Negligible

amounts of AFCA was seen after electrolysis however, current densities were very poor. XPS measurements before and after the chronoamperometry (**Figure 5.8.3**) revealed that Mn came off the electrode surface during the reaction, further suggested by a dark pink colouring on the tubes connecting the pump to the cell. This adds further support for the need to use more stable electrocatalysts for the oxidation reaction, for this amino acid synthesis to become viable in acidic electrolytes.

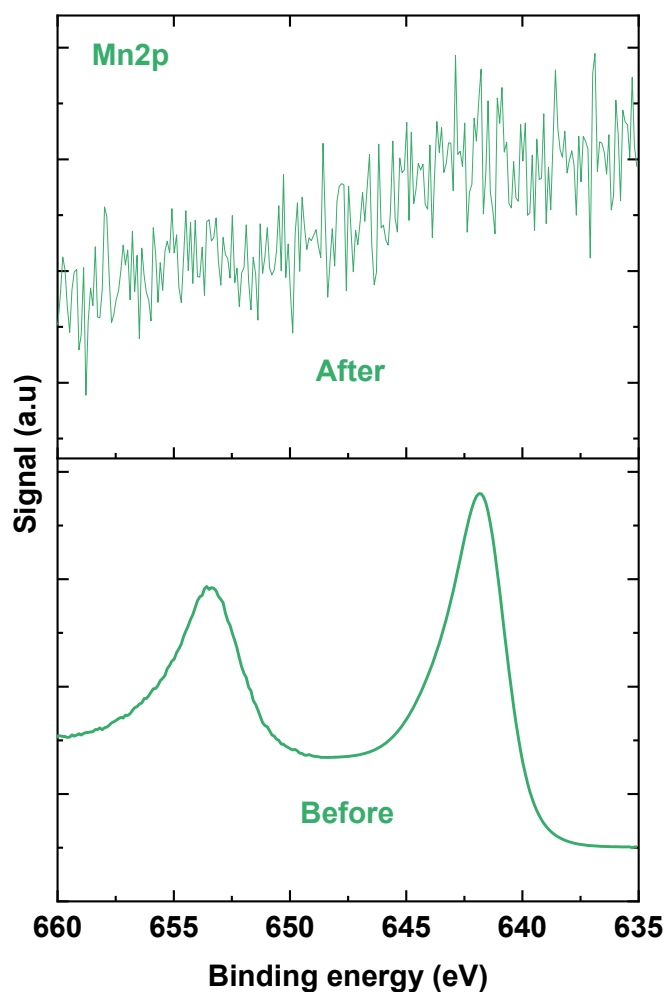
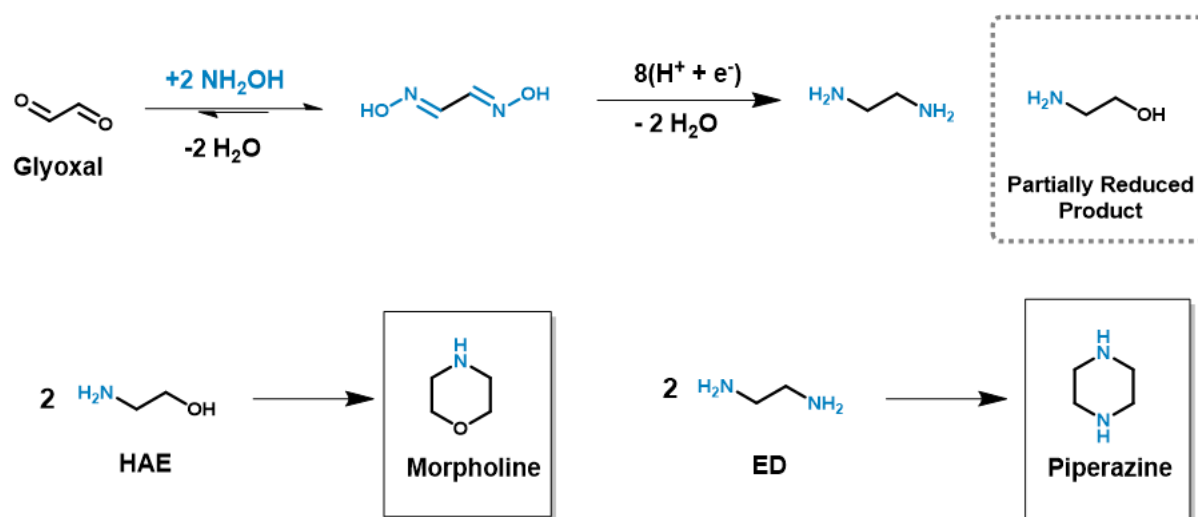


Figure 5.8.3. Mn2p core level XPS spectra of MnO_x anodes before and after chronoamperometry using MEA configuration. Reaction condition: 0.1 M HClO₄ (pH 1), 1.835 V cell potential for 10 h, 30 mM HMFA. XPS sample was taken by Yuxiang Zhou, and analysed by myself.

5.9 Towards the Electrochemical Synthesis of 1,2-Diamines

Many of the important amines used in industry are non-aromatic heterocycles such as piperazine and morpholine, which have uses in dyes and pharmaceuticals.^{239,240} The conditions behind electrochemical reductive amination in the previous section can also apply to straight-chain aldehydes available from biomass, such as glyoxal. The complete reductive amination of glyoxal results in the production of ethylenediamine (ED), with the partially aminated product potentially yielding 2-hydroxyaminoethane (HAE). These compounds can be used to produce various polyamides or can be dimerised themselves to form useful heterocycles (**Scheme 5.9.1**). A potential method of controlling selectivity can be possible by only using one equivalent of NH_2OH if we wish to target HAE as the major product, although this was not investigated.



Scheme 5.9.1. Formation of aliphatic amines and corresponding heterocycles via electrochemical reductive amination from glyoxal.

Like the electrochemical amination of furanic compounds, Ag electrodes showed activity for glyoxal reductive amination in acidic pH, with ethylene diamine being detected as the major organic product with about 50% FE at -0.50 V vs RHE (**Figure 5.9.1**).

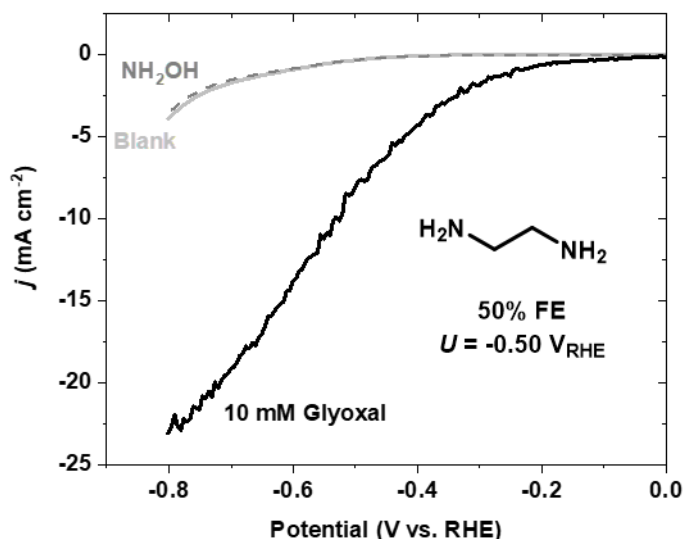
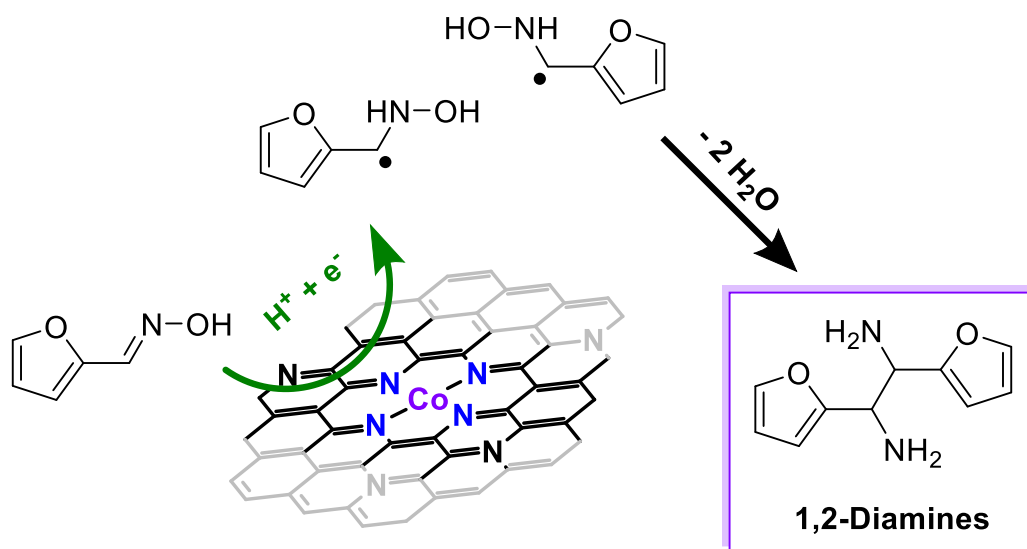


Figure 5.9.1. LSVs of Ag electrodes before and after the addition of 20 mM NH_2OH and 10 mM glyoxal (2:1 equivalents). Reaction conditions: 0.1 M HClO_4 electrolyte. The scan rate was 50 mV s^{-1} and was scanned in the cathodic direction.

The work in Chapter 4 showed it was possible to couple furfural together under cathodic potentials using single-atom catalysts to produce a diol species – hydrofuroin in the case of furfural. Inspired by this result, it was hypothesised that a reaction analogous to this is possible starting with oximes instead of carbonyl species which can produce 1,2-diamines under similar conditions (**Scheme 5.9.2**). As a starting point, CoTAP was chosen as the preferred electrode material as it showed the highest efficiency for hydrofuroin production with low amounts of organic side products.



Scheme 5.9.2. Electrochemical synthesis of 1,2-diamines on CoTAP cathodes starting from furfural and hydroxylamine.

Figure 5.9.2 shows the LSVs of CoTAP, TAP and carbon black (Ketjen Black EC-600JD, KB) electrodes before and after the addition of 15 mM furfural and NH_2OH . It was already shown that acidic media is preferred for the amination of furfural into FA, with hardly any activity at pH 10 even using favourable Ag electrodes, signalling that reductive amination is not preferred at this pH. Consequently, a weakly furfural-binding electrode such as carbon is not likely to reduce the oxime into the amine even at pH 1, and even more unlikely so at pH 10. Interestingly, it is seen that on all three carbon-based electrodes, a large increase in current density is seen relative to the blank electrolyte LSV. The only reasonable explanation that can explain this property is a single-electron and proton transfer, as opposed to the reductive amination process into the amine, which is unlikely under these conditions. It is therefore likely that oxime radical species form that couple together to form a 1,2-diamine species after the elimination of water.

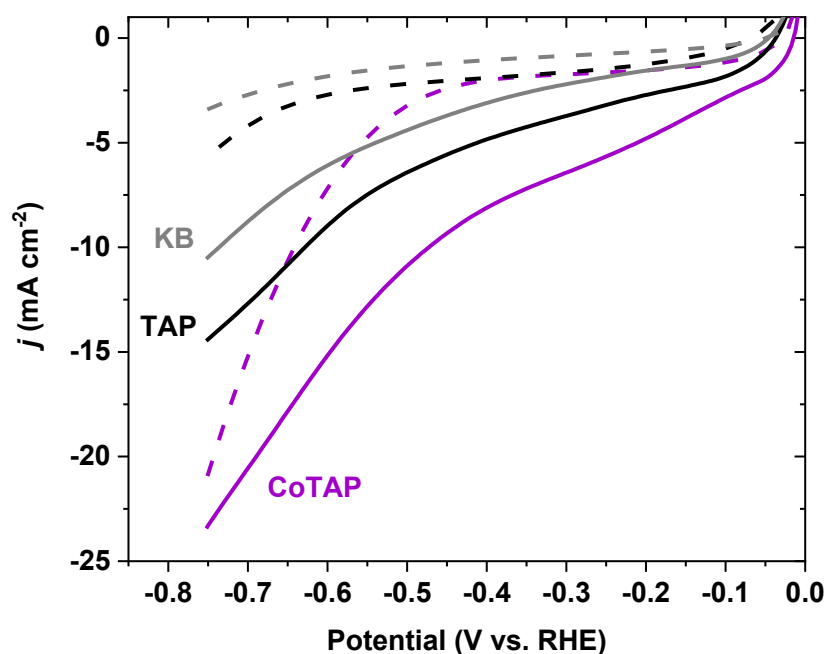


Figure 5.9.2. LSVs of different carbon-based cathode materials before (dashed line) and after (solid line) the addition of 15 mM furfural and 1:1 equivalents of NH_2OH (15 mM). Reaction conditions: 0.1 M potassium bicarbonate-carbonate buffer electrolyte (pH 10), catalyst loading was 0.4 mg cm^{-2} . The scan rate was 50 mV s^{-1} and was scanned in the cathodic direction.

A greater current is seen using CoTAP compared to the KB control and blank TAP, which suggests that the central Co atom plays an important role in increasing reduction activity; analogous to the conclusions observed during hydrofuroin formation in Chapter 4. The presence of diamine species was not detected using NMR because of the difficulty in distinguishing between the diastereomers produced. To solve this issue, quantification using LC-MS is currently underway.

5.11 Conclusion

The incorporation of nitrogen moieties into platform chemicals was demonstrated in this chapter, which expanded the number of valuable chemicals possible from biomass electrovalorisation. The lack of inherent nitrogen moieties in lignocellulosic biomass was addressed by using NH_2OH as a cheap external nitrogen source, that produces oxime intermediates which can be reduced electrochemically into amines. Various metal surfaces were tested for their reduction activity, leading to the conclusion that Ag electrodes were the most efficient for this. Using DFT calculations, a mechanistic insight was presented showing the most feasible route for amination only had one slightly endothermic step, with Ag being able to facilitate the reduction of this intermediate even when simulated at 0 V vs RHE. During optimisation, the electrolyte pH was shown to have a significant effect on the efficiency of the reduction reaction, with the optimal pH for the reaction being about pH 1, with reduction activity almost ceasing in alkaline pH, suggesting that the protonated version of the oxime is required for efficient reductive amination.

An example of a multi-step electrosynthesis was achieved resulting in the production of a biobased amino acid, AFCA, starting from HMF. The process achieved up to 69% FE for the reductive amination reaction, and 35% for the oxidation of the resultant HMFA to AFCA using MnO_x anodes which can be done in the same electrolyte, mitigating the need to separate intermediates before subsequent reactions. However, the stability of the MnO_x electrodes needs to be addressed before an industrial scale-up of this process.

As an extension to the results in Chapter 4, the radical coupling on CoTAP single-atom catalysts was tested as an alternative method to produce 1,2-diamines. A large amount of reduction activity was seen in a mildly alkaline electrolyte, attributed to a single-electron transfer to produce the radical which can couple to produce the diamine. Product quantification for this section is still underway but electrochemical data shows promise for a new method of electrochemical production of amines.

A scale-up for the electrochemical production of aminated compounds was attempted during the continuous electrochemical reductive amination of HMF using an MEA configuration. AgNPs displayed the highest activity for HMFA production with reasonable current densities and FEs of 27% when using IrO_x counter electrodes. The subsequent oxidation of HMFA to produce AFCA in the MEA was attempted with less success, due to the instability of MnO_x under these conditions. More work needs to be done to optimise the MEA which will be the focus of further work in this area.

Appendix B

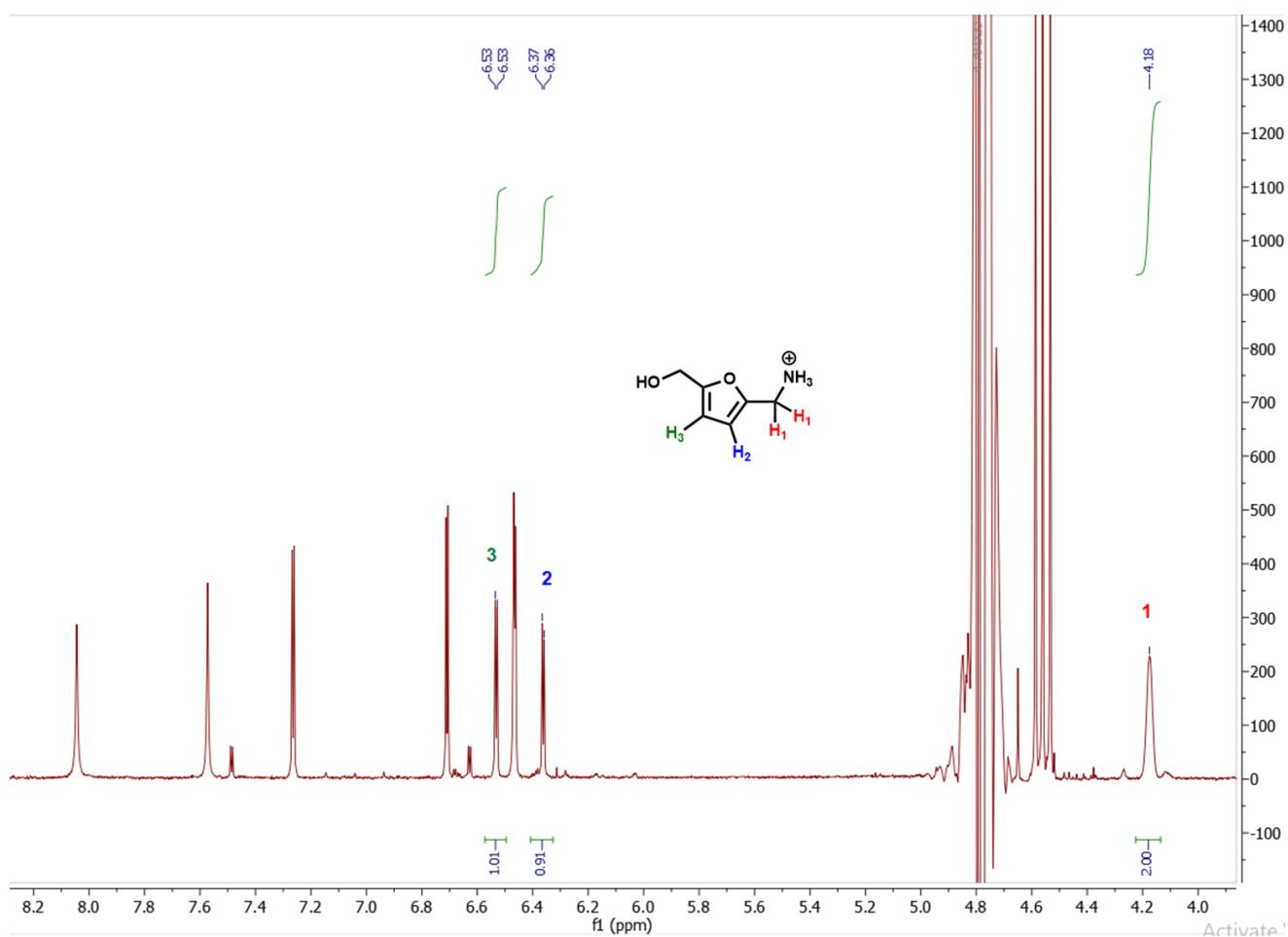


Figure B1. ^1H NOESY water suppression NMR (400 MHz, H_2O), spectrum of electrolyte post electrolysis of HMF reductive amination on Ag cathodes. Reaction conditions: spectrum was taken in 0.1 M HClO_4 solution (pH 1), 10 mM HMF and NH_2OH . Applied potential was -0.50 V vs RHE for 3.5 hours on an Ag foil working electrode.

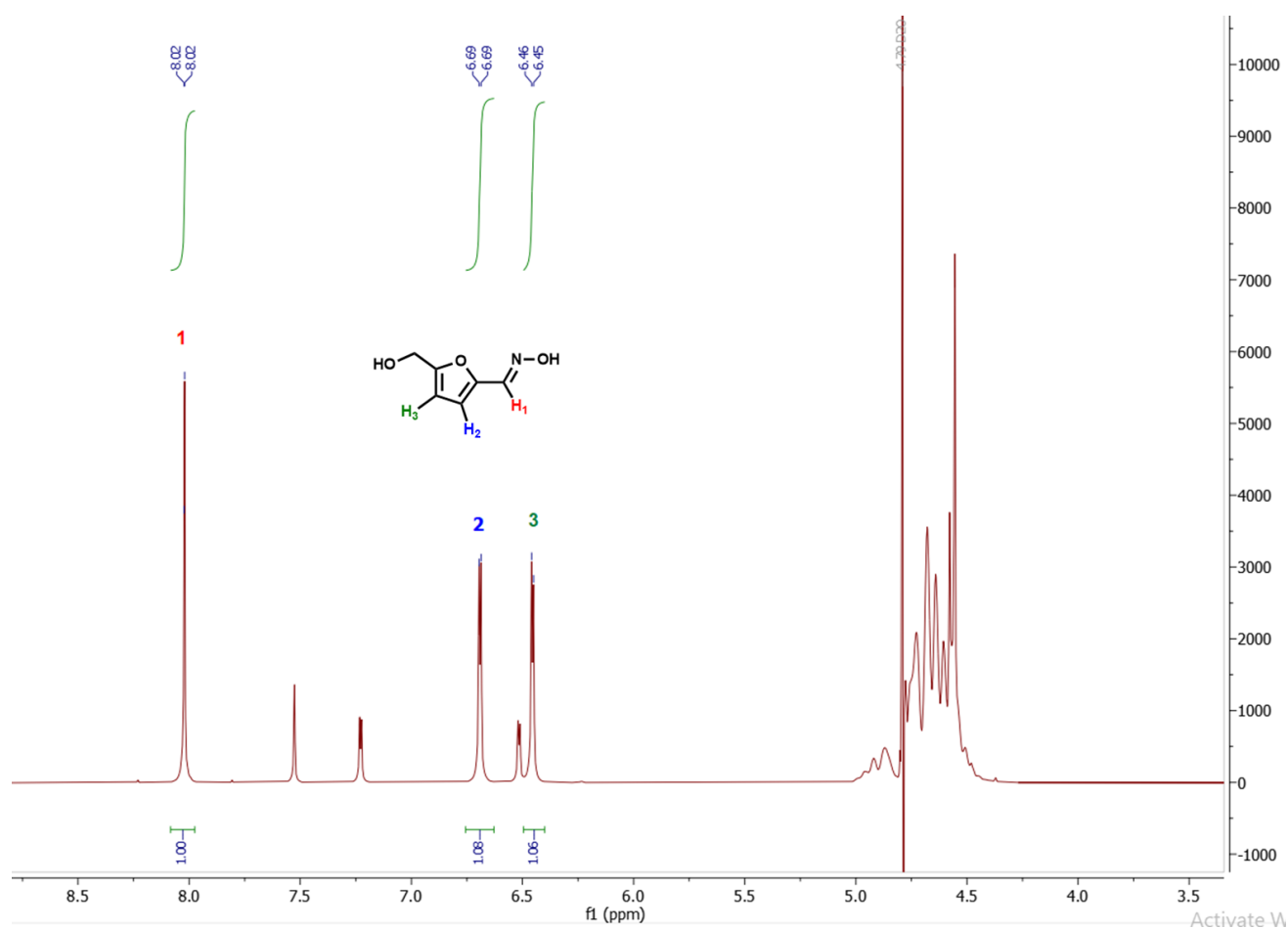


Figure B2. ^1H NOESY water suppression NMR (400 MHz, H_2O), spectrum of 20 mM HMF mixed with 20 mM NH_2OH before electrolysis. Spectrum was taken in MilliQ water. The peaks between 7.25 – 7.50 ppm are likely due to the E/Z isomers formed from the resultant oxime.

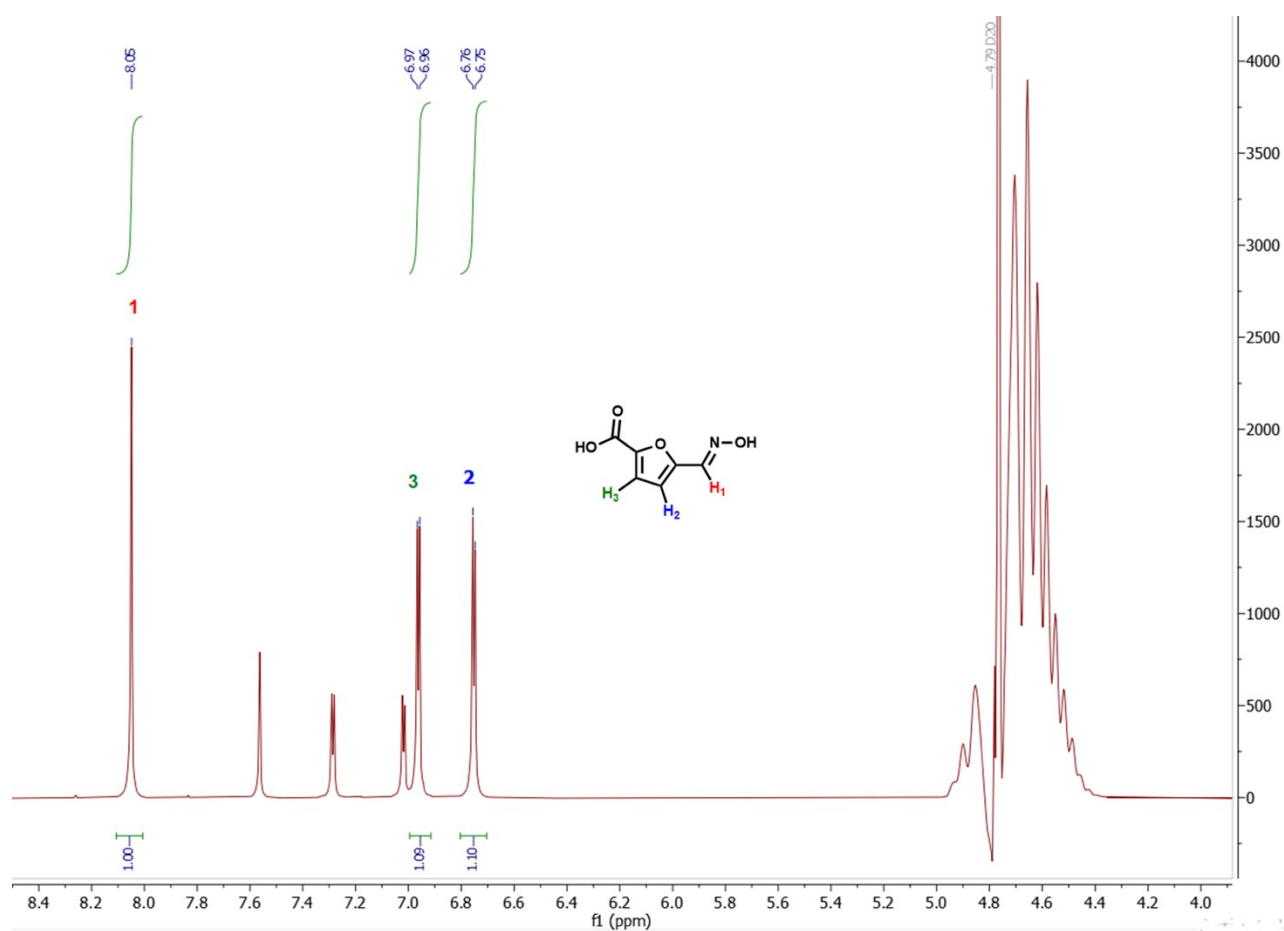


Figure B3. ¹H NOESY water suppression NMR (400 MHz, H₂O), spectrum of 20 mM FFCA mixed with 20 mM NH₂OH before electrolysis. Spectrum was taken in MilliQ water. The peaks between 7.25 – 7.60 ppm are likely due to the E/Z isomers formed from the resultant oxime.

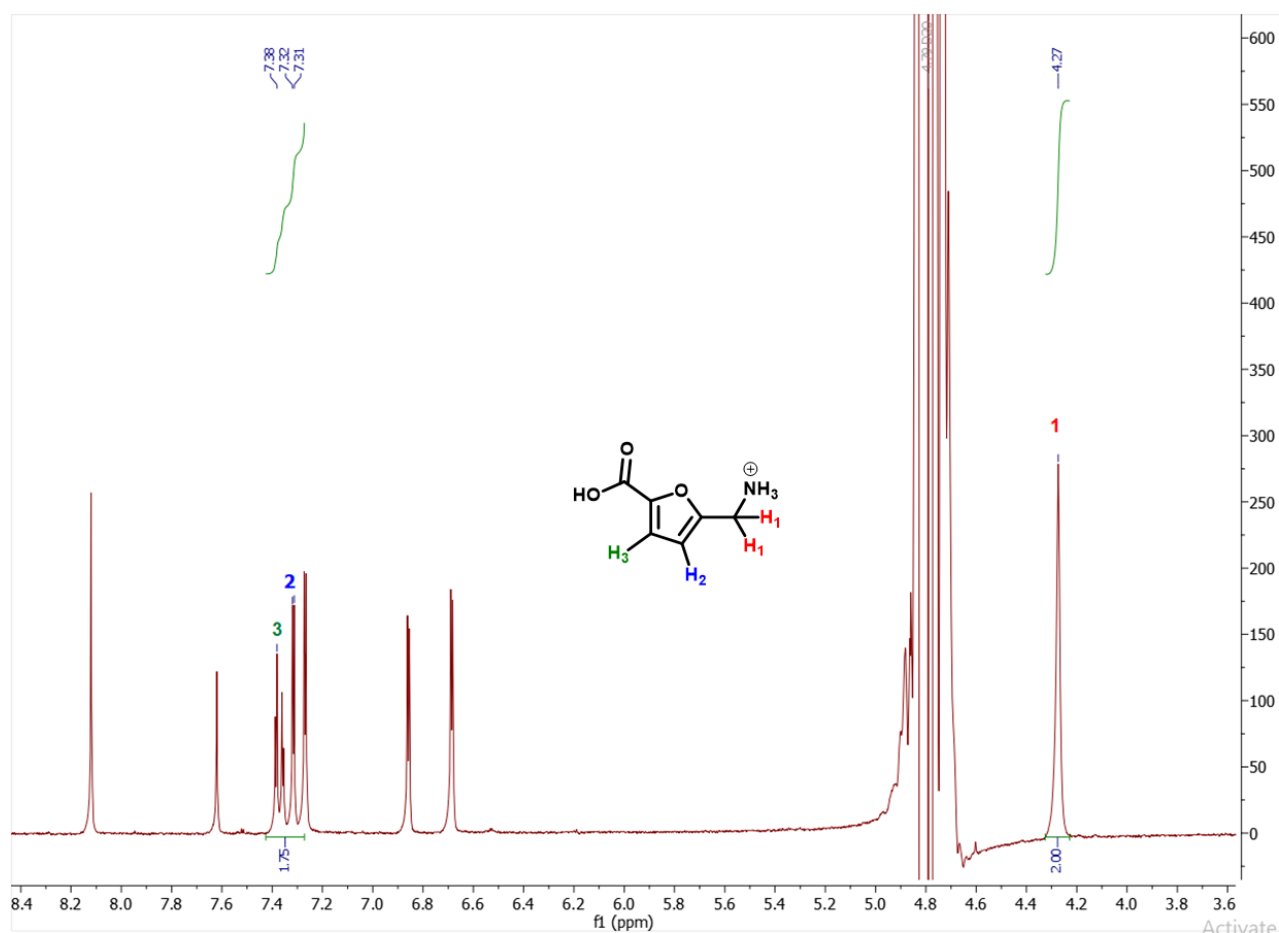


Figure B4. ¹H NOESY water suppression NMR (400 MHz, H₂O), spectrum of electrolyte post electrolysis of FFCA amination on Ag cathodes. Spectrum was taken in 0.1 M HClO₄ solution (pH 1) post electrolysis. Reaction conditions: 0.1 M HClO₄ electrolyte, 10 mM FFCA and NH₂OH. Applied potential was -0.50 V vs RHE for 3.5 hours on an Ag foil working electrode.

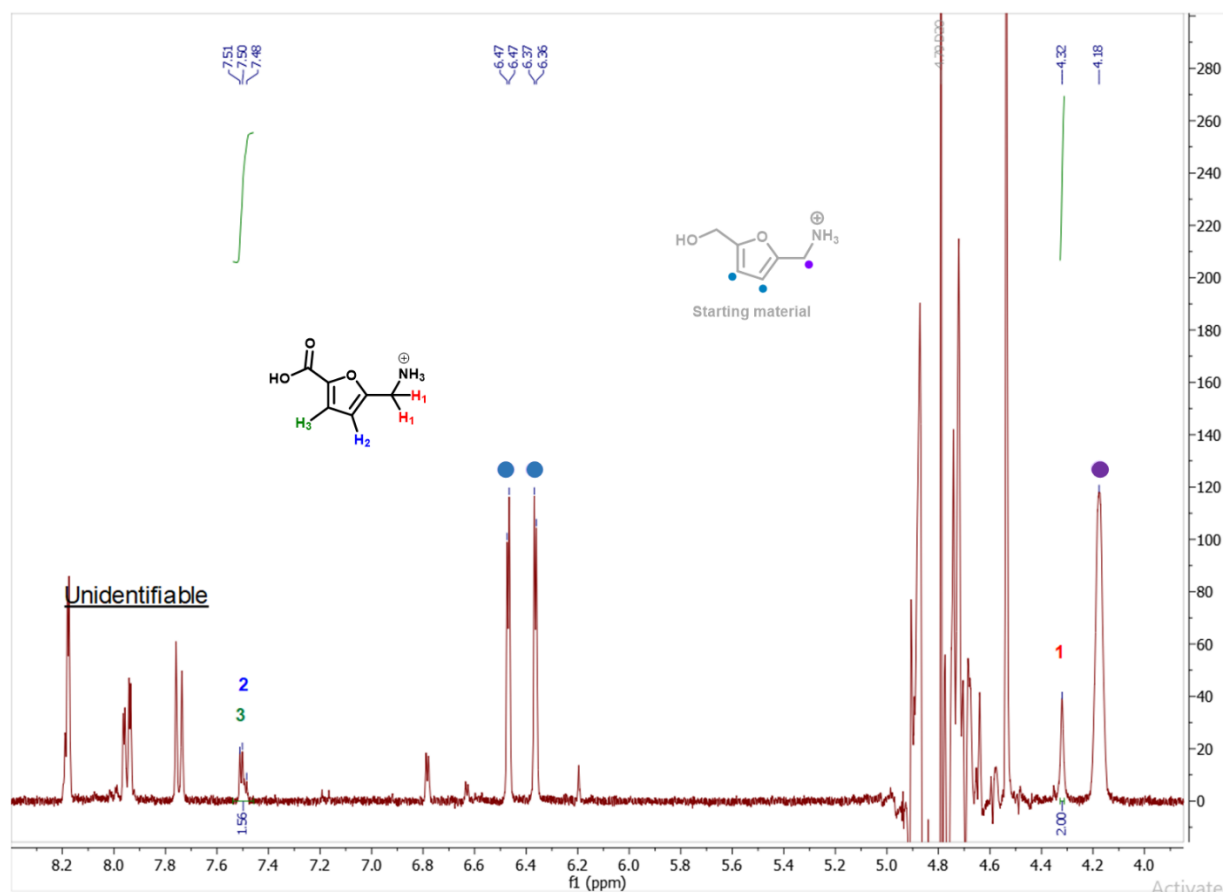


Figure B5. ^1H NOESY water suppression NMR (400 MHz, H_2O), spectrum of electrolyte post electrolysis of HMFA oxidation on MnO_x electrodes. Spectrum was taken in 0.1 M HClO_4 solution (pH 1) post electrolysis. Reaction conditions: 0.1 M HClO_4 electrolyte, 10 mM HMFA. Applied potential was 1.60 V vs RHE for 3.5 hours.

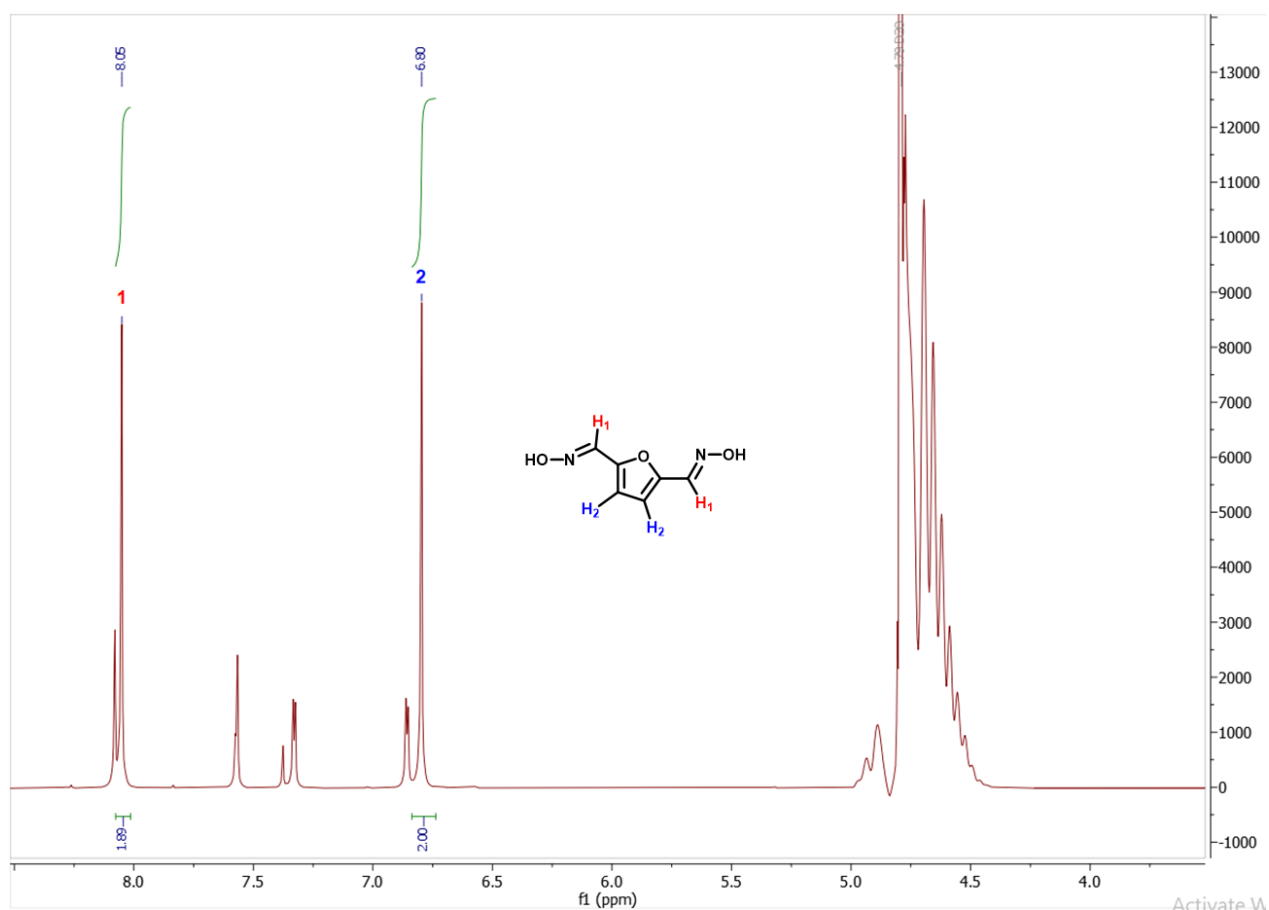


Figure B6. ¹H NOESY water suppression NMR (400 MHz, H₂O), spectrum of 20 mM DFF mixed with 40 mM NH₂OH (1:2 equivalent ratio). Spectrum was taken in MilliQ water. The peaks between 7.25 – 7.60 ppm are likely due to the E/Z isomers formed from the resultant oximes.

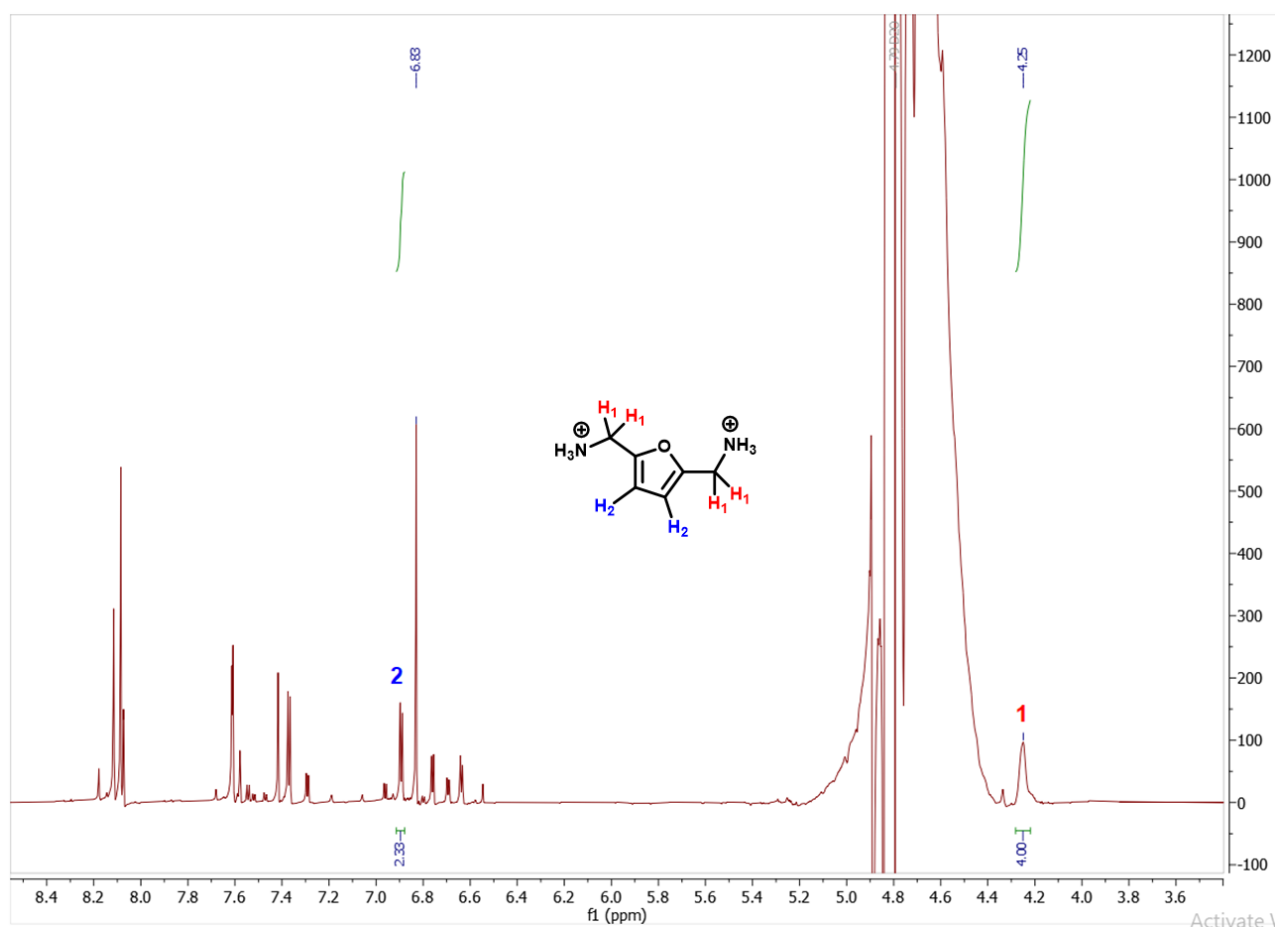


Figure B7. ¹H NOESY water suppression NMR (400 MHz, H₂O), spectrum of electrolyte post electrolysis of DFF amination on Ag electrodes. Spectrum was taken in 0.1 M HClO₄ solution (pH 1) post electrolysis. Reaction conditions: 0.1 M HClO₄ electrolyte, 10 mM DFF and 20 mM NH₂OH. Applied potential was -0.50 V vs RHE for 3.5 hours on an Ag foil working electrode.

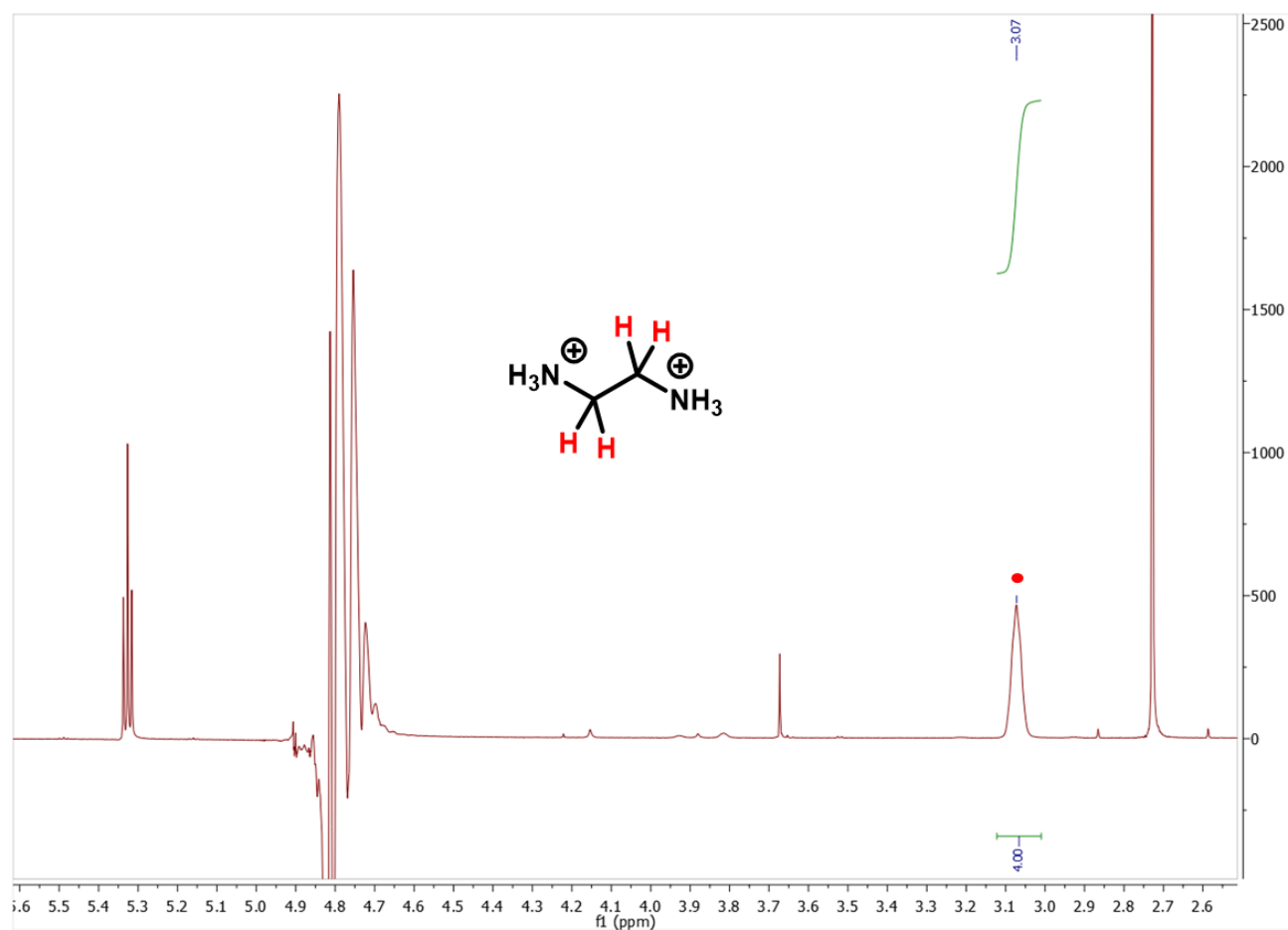


Figure B8. ¹H NOESY water suppression NMR (400 MHz, H₂O), spectrum of electrolyte post electrolysis of glyoxal amination on Ag electrodes. Spectrum was taken in 0.1 M HClO₄ solution (pH 1) post electrolysis. Reaction conditions: 0.1 M HClO₄ electrolyte, 10 mM glyoxal and 20 mM NH₂OH. Applied potential was -0.50 V vs RHE for 3.5 hours on an Ag foil working electrode.

6 | Heterogenous Electrochemical Oxidation using TEMPO Catalysts

The contents of this chapter were the result of the author of this thesis, and contributions from other people are clearly stated throughout the chapter where appropriate. In short, the NDI organic catalysts used in this chapter were synthesised and characterised by Dr Matthew Bidwell. Caiwu Liang was present during all operando optical spectroscopy measurements. Yuxiang Zhou helped conduct the EC-MS experiments with the aid of Dr Soren B. Scott. XPS measurements were carried out by Yuxiang Zhou and analysed by the author of this thesis.

6.1 Objective and Motivation

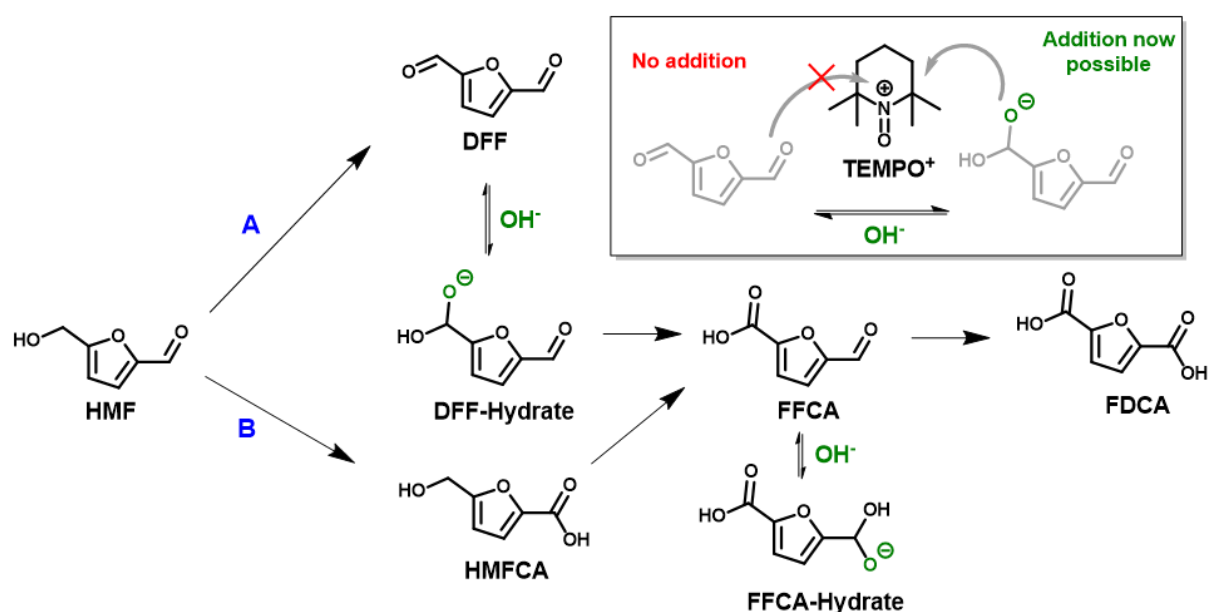
As mentioned in Chapters 1 and 2, polymers are some of the most produced chemicals in the world, with methods surrounding their disposal being the subject of major environmental considerations. Chapter 6 explores the electrochemical oxidation of HMF into 2,5-furandicarboxylic acid (FDCA), which is a promising replacement monomer for terephthalic acid in PET. This dicarboxylic acid can effectively be entirely sourced from biomass, and can be polymerised with ethylene glycol resulting in the condensation polymer PEF, which has better thermochemical properties than PET and has attracted attention for use in beverage packing.³⁴ The stable nitroxyl radical TEMPO has been demonstrated to complete the electrochemical oxidation of HMF to FDCA with almost 100% FE when used in a homogeneous solution;¹⁵⁰ however, a limitation arises whereby TEMPO needs to be separated post electrolysis, which can be a reagent heavy process. This chapter introduces a novel approach in which TEMPO can be immobilised on an electrode surface for use as a heterogeneous electrocatalyst using both covalent and non-covalent means.

The underlying mechanisms of the electrooxidation of HMF using immobilised TEMPO have not yet been studied in detail and are analysed in this chapter using a combination of XPS, cyclic voltammetry, UV-Vis spectroscopy, and *operando* optical spectroscopy. To determine the stability of the produced TEMPO catalysts, electrochemistry-mass spectrometry is used to probe the degradation under working potentials, and from this, predictions on catalyst life are calculated for the eventual use in an industrial electrolyser to produce FDCA.

To open avenues for the commercialisation of this process, optimisation of the synthesised catalysts is carried out by testing the effect of reaction parameters such as catalyst loading, HMF concentration, pH, and types of carbon supports. A proposed scale-up and commercialisation for this process is presented for the continuous production of FDCA, using a heterogeneous TEMPO catalyst for the first time in recorded literature. The results from this chapter will provide important insights into the development of electrosynthesis.

6.2 TEMPO and HMF Oxidation

Of all the reactions involved in the electrochemical biorefinery, alcohol oxidation is one of the most significant due to the relative abundance of naturally occurring alcohols from biomass. Platform chemicals which contain primary alcohols can be electrochemically oxidised to produce corresponding carboxylic acids which can be used in renewable polymers. This is relevant for the oxidation of HMF into FDCA whereby the resultant dicarboxylic acid can replace terephthalic acid in PET. An ideal alcohol oxidation electrocatalyst needs to be cheap, non-toxic, selective and produce high current densities. One molecule which fits these criteria is TEMPO – a stable metal-free nitroxyl radical made from the ubiquitous elements nitrogen, carbon, hydrogen, and oxygen. As depicted in Chapter 2, the mechanism of electrochemical alcohol oxidation using TEMPO is an indirect oxidation that involves applying a potential to oxidise the radical to an oxoammonium cation (TEMPO^+), which can facilitate the nucleophilic addition of an alcohol group for further oxidation steps (**Figure 2.2.6**). The partial oxidation of primary alcohols also can yield aldehydes, which can be further oxidised into a carboxylic acid after the addition of an OH^- across the carbonyl bond to form a deprotonated hydrate, which can go through the TEMPO catalytic cycle again to form the carboxylic acid functional group. It is possible that this addition step may be rate-limiting, which could be increased by deprotonating the alcohol making it into a better nucleophile. Similarly, the addition of OH^- ions to aldehyde groups to produce hydrates which can increase FDCA production rates because the alkoxides will be able to add onto TEMPO^+ species. For these reasons, the electrochemical alcohol oxidation studied in this chapter are conducted in alkaline electrolytes. A scheme of HMF oxidation to produce FDCA is depicted in **Scheme 6.2.1**, highlighting the importance of OH^- ions for producing FDCA.



Scheme 6.2.1. HMF oxidation pathways in alkaline electrolyte. Deprotonated hydrates are a necessary step for aldehyde oxidation using TEMPO.

A mild pH 10 potassium bicarbonate-carbonate buffer was tested for HMF oxidation activity using TEMPO in a homogenous solution, which confirmed the reproducibility of earlier work.¹⁵⁰ The liquid products obtained after 2 h at 1.40 V vs RHE TEMPO yielded FDCA with FEs and selectivities above 99% on carbon electrodes (**Figure C1**). Whilst high FEs (~99%) for FDCA are obtained, an industrial scale-up should aim to avoid using TEMPO as a homogenous catalyst because of the reagent-heavy chromatography techniques required to separate the FDCA from the TEMPO and electrolyte. Hence, it would be beneficial to immobilise TEMPO on the surface of the electrode (**Figure 6.2.1b**). The benefits of immobilising TEMPO to produce a heterogenous catalysis process include:

- **Easier methods of purification** – no solvents will be needed to separate TEMPO from the electrolyte after chronoamperometry experiments. FDCA is soluble in alkaline pH but precipitates out in acidic pH therefore can be separated simply by altering the pH at the end of the reaction.
- **Mitigating processes which deactivate TEMPO** – single electron transfers may result in radical formation which can dimerise and deactivate TEMPO molecules. Immobilisation will prevent the radical species from freely moving and coupling with each other. Impurities dissolved in the electrolyte are also less likely to deactivate the catalyst.
- **Use in both organic and aqueous electrolytes** – catalysts which are insoluble in aqueous electrolytes such as sp^2 carbon frameworks, can be adsorbed onto carbon electrodes and used as an electrocatalyst.
- **More efficient routes of electron transfer** – a smaller distance between the catalyst and electron source will improve rates of electron transfer and hence improve current densities.

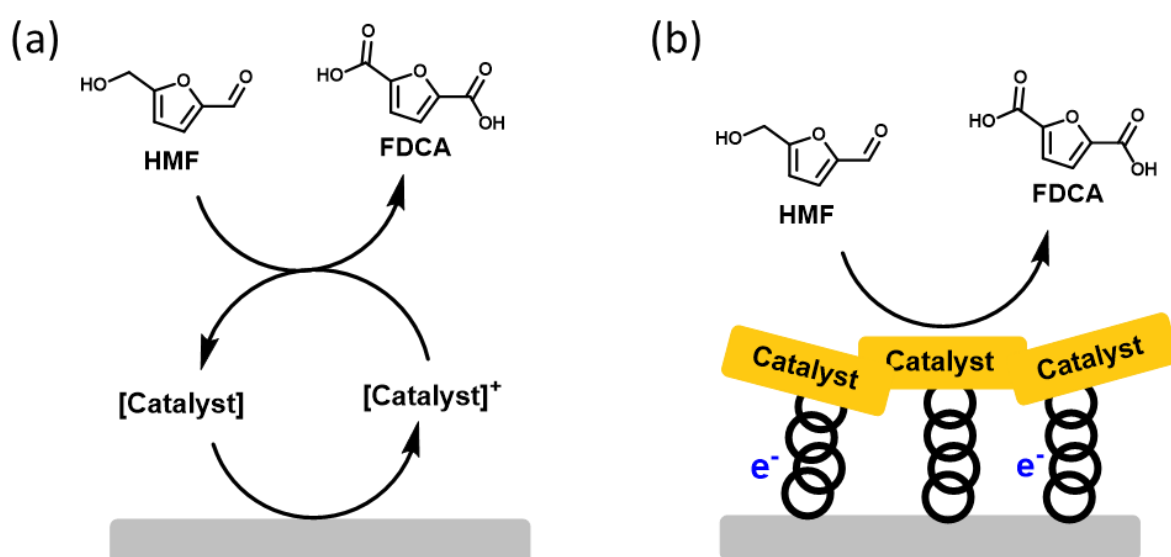


Figure 6.2.1. Methods of electrocatalysis for HMF oxidation. (a) homogenous catalysis and (b) immobilised catalyst for HMF oxidation.

6.3 Strategies for TEMPO Immobilisation

TEMPO immobilisation onto an electrode surface can occur via a covalent or non-covalent route. Both methods were explored, first by using amide linkages to attach TEMPO to MWCNT sidewalls (covalent immobilisation), and then by attaching TEMPO onto aromatic cores followed by physisorption onto carbon electrodes (non-covalent immobilisation). The covalently immobilised TEMPO-MWCNTs were active towards HMF oxidation (**Figure 6.3.1a**), however, the oxidation current decreased rapidly during constant potential experiments and no HMF oxidation products were observed at 1.45 V vs RHE. It is likely that the amide linkages are susceptible to hydrolysis under oxidising potentials so are to be avoided. XPS measurements before and after chronoamperometry (**Figure 6.3.1b & c**) revealed that the amide linkage was breaking under these potentials and hence covalent linkages were not further studied for this project.

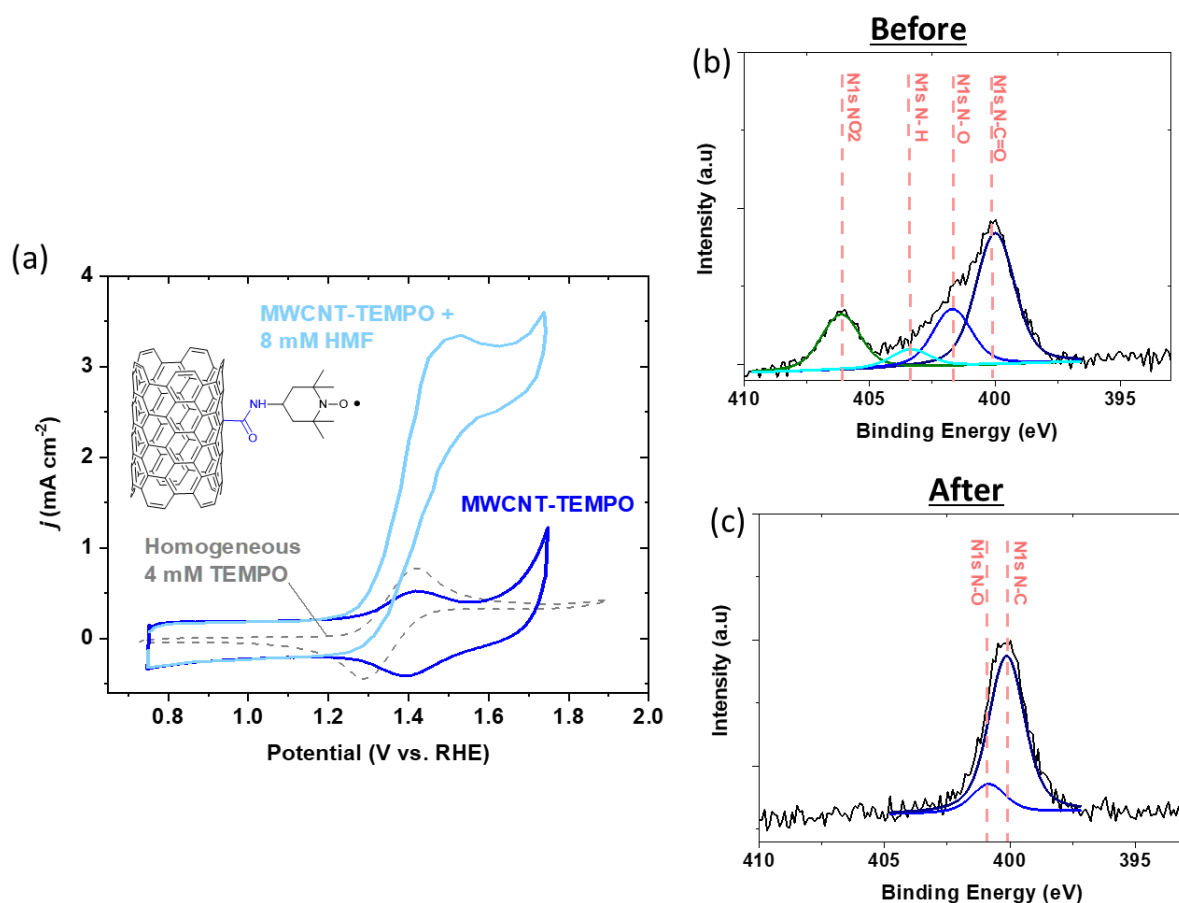


Figure 6.3.1. Electrochemical oxidation activity of TEMPO-MWCNTs. (a) CVs of MWCNT-TEMPO before and after the addition of 8 mM HMF, compared to 4 mM of homogeneous TEMPO. (b) N1s core level XPS spectra before electrolysis and (c) after electrolysis. Reaction conditions: 0.1 M potassium bicarbonate-carbonate buffer (pH 10), 8 mM HMF, chronoamperometry done at 1.40 V vs RHE, TEMPO-MWCNT loading was 0.2 mg cm⁻². The scan rate was 50 mV s⁻¹.

Physisorption of TEMPO onto carbon electrodes through π - π stacking was explored as an alternative to covalent TEMPO linkages. Aromatic cores can result in an intimate π - π stacking onto graphitic carbon supports. We hypothesised that naphthalene diimide (NDI) molecules would provide a stable framework for TEMPO immobilisation because the imide linkages attaching the TEMPO to the core are delocalised into the aromatic core, making oxidative degradation of the catalyst less feasible. A library of compounds with increasing TEMPO moieties was produced and all the catalysts used in this study are displayed in **Figure 6.3.2**. It was hypothesised that by increasing the amount of TEMPO moieties per unit surface area, the greater this would increase the HMF oxidation activity as more active TEMPO⁺ moieties would be present under anodic potentials. The NDI catalysts are also very hydrophobic, which helps the catalyst better adhere to the electrode as opposed to dissolving in the aqueous electrolyte; however, this becomes a balancing act as adding more TEMPO moieties decreases the molecule's hydrophobicity which can promote catalyst dissolution.

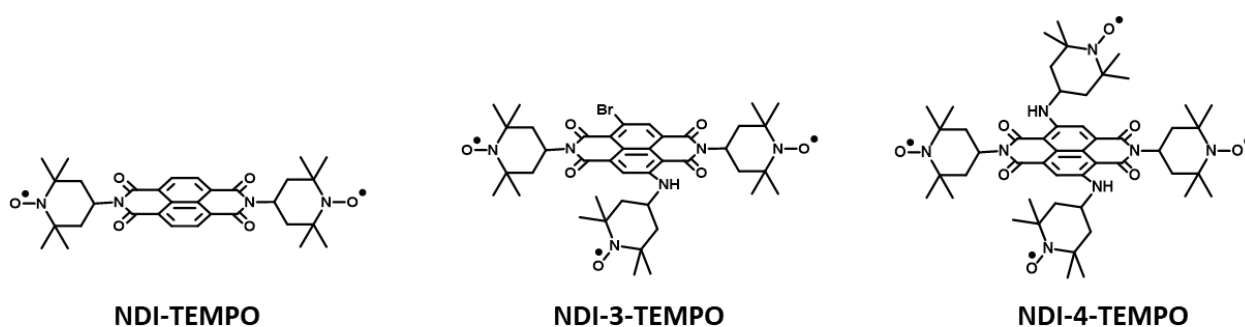


Figure 6.3.2. TEMPO catalysts that are synthesised and used in this chapter. Catalysts were synthesised by Dr Matthew Bidwell.

Before electrochemical testing, the catalysts were physisorbed onto various graphitic carbon supports including VCX-72, MWCNTs, and KB, to increase their conductivities and total surface area. Due to the deep colouring of these catalysts in solution, it is possible to observe the maximum amounts of catalyst that can physisorb onto different carbon supports through calorimetric methods by studying the concentration of catalyst left in solution after sonication. **Figure 6.3.3** shows a solution of 50 mM NDI-4-TEMPO in acetone before and after 1 hour of sonication and filtration, with just 1 mg of VCX-72 carbon black. The solution visibly gets lighter in colour signalling the NDI-4-TEMPO is stacking onto the surface of the carbon which can be used to accurately determine the catalyst loading of electrodes. An idea for a future study is to study the optimal NDI-TEMPO loading on each catalyst and carbon support, as they will likely have a different maximum amount of catalyst: carbon ratio. Instead, a moderate 1:1 weight ratio of catalyst to carbon was used for all experiments unless stated otherwise.

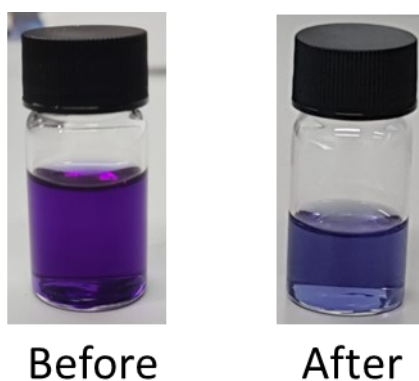


Figure 6.3.3. A solution of 50 mM NDI-4-TEMPO before and after 1 h sonication with 1 mg of carbon black (VCX-72).

6.4 The Cannizzaro Reaction

It is important to consider the potential side reactions which could occur during HMF oxidation both via electrochemical and non-electrochemical means. Of the non-electrochemical reactions, the most prominent side reaction is the Cannizzaro reaction – a disproportionation reaction where aldehyde groups can react with one another to form a carboxylic acid and alcohol (**Figure 2.2.3**), which is catalysed by OH^- . HMF can also degrade into humin products under strongly alkaline conditions¹⁴⁰ which can result in catalyst poisoning from the resultant humins. Unfortunately, it is difficult to avoid alkaline conditions for HMF oxidation because the formation of a hydrate species requires OH^- to form the reactive alkoxide needed to later produce FDCA. The rate of the Cannizzaro reaction on 20 mM HMF and FFCA, in pH 1, 10 and 13 solutions after 24 h (**Figure 6.4.1**) was explored to determine the extent of degradation issues that will be present because of the Cannizzaro reaction. From the HPLC chromatograms, the HMF solutions in pH 10 and pH 1 show no significant reduction of the HMF peak, whereas the peak in pH 13 shows a noticeable reduction in HMF alongside a small increase in the amount of FFCA and an even smaller increase in DFF and FDCA. For the FFCA solutions, a similar trend is seen whereby pH 1 and 10 show little FFCA degradation, but pH 13 shows an increase in FDCA produced after 24 h. A mild pH 10 electrolyte is, therefore, an ideal pH for this reaction, as it lowers the degradation rate of HMF via the Cannizzaro reaction, whilst still providing necessary OH^- ions needed for the oxidation. The fact that FDCA is produced via the Cannizzaro reaction can aid us to increase the yield of FDCA from a reaction, should issues arise in electrochemically oxidising FFCA into FDCA.

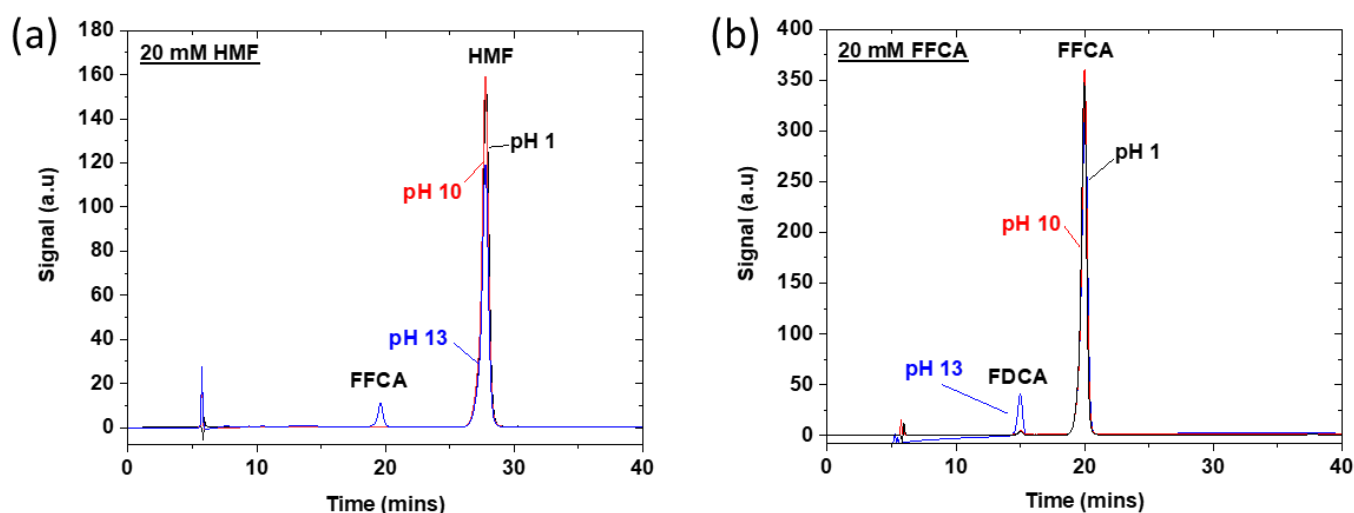


Figure 6.4.1. HPLC chromatograms of 20 mM (a) HMF and (b) FFCA exploring the Cannizaro reaction in pH 1, 10, and 13. pH 1, 10, and 13 solutions were 0.1 M HClO_4 , 0.1 M potassium bicarbonate buffer, and 0.1 M KOH respectively, and the solutions were left unstirred at room temperature for 24 h.

6.5 Electrochemical Oxidation Activity of NDI Catalysts

In a pH 10 potassium bicarbonate electrolyte, NDI-TEMPO, NDI-3-TEMPO, and NDI-4-TEMPO all showed excellent activity (**Figure 6.5.1a**) for oxidising HMF and have comparable current densities to 4 mM homogeneous TEMPO even at a low loading of 0.3 mg cm^{-2} (**Appendix Figure C2**). This is likely due to a more efficient route for electron transfer when the TEMPO is attached to the electrode surface, compared to mass transport limitations involved in using homogeneous TEMPO when dissolved in the electrolyte. The blank cycles differ for all three catalysts, with NDI-3-TEMPO and NDI-4-TEMPO displaying higher current densities than NDI-TEMPO. This is expected as these catalysts have a higher density of TEMPO moieties per unit mass of catalyst. For constant potential experiments, the catalyst loading was increased to 2 mg cm^{-2} and a low concentration of 5 mM HMF was used as a starting substrate, aiming to produce FDCA with a 100% conversion. However, only about 108 C out of the theoretical 175 C required to oxidise 5 mM HMF into FDCA was able to be passed over 10 hours using NDI-TEMPO at 1.45 V vs RHE, until the current became too small for reasonable complete oxidation ($<0.1 \text{ mA cm}^{-2}$). This signalled that either no more biomass oxidation was occurring or that the catalyst had completely degraded. FFCA and FDCA were detected as the main organic product with FEs of 75% and 8%, respectively. Similar experiments with NDI-3-TEMPO and NDI-4-TEMPO resulted in a slightly higher charge being able to be passed, with 120 C passed out of the theoretical 175 C needed before the currents got too small for a reasonable timely completion. Interestingly,

FDCA was produced with much greater FE of up to 45% FE using NDI-4-TEMPO, and almost the same amount on NDI-3-TEMPO (**Figure 6.5.1b**). This adds some merit to the earlier hypothesis of packing as much TEMPO on the surface as possible to increase rates of oxidation is a method of improving efficiency, or that the TEMPO moieties on the sides of the molecule behave differently from the ones attached using imide bonds.

An initial observation is that the final step of oxidation from FFCA $\rightarrow$ FDCA is quite sluggish under these conditions. That said, we have effectively produced an electrocatalyst (NDI-TEMPO) which results in the selective production of FFCA – a first-of-its-kind. FFCA is a useful furanic compound which can undergo reductive amination to form the amino acid AFCA, which can undergo self-polymerisation to form a renewable polyamide which was studied in Chapter 5, but also has its own uses in polymers.²³⁵

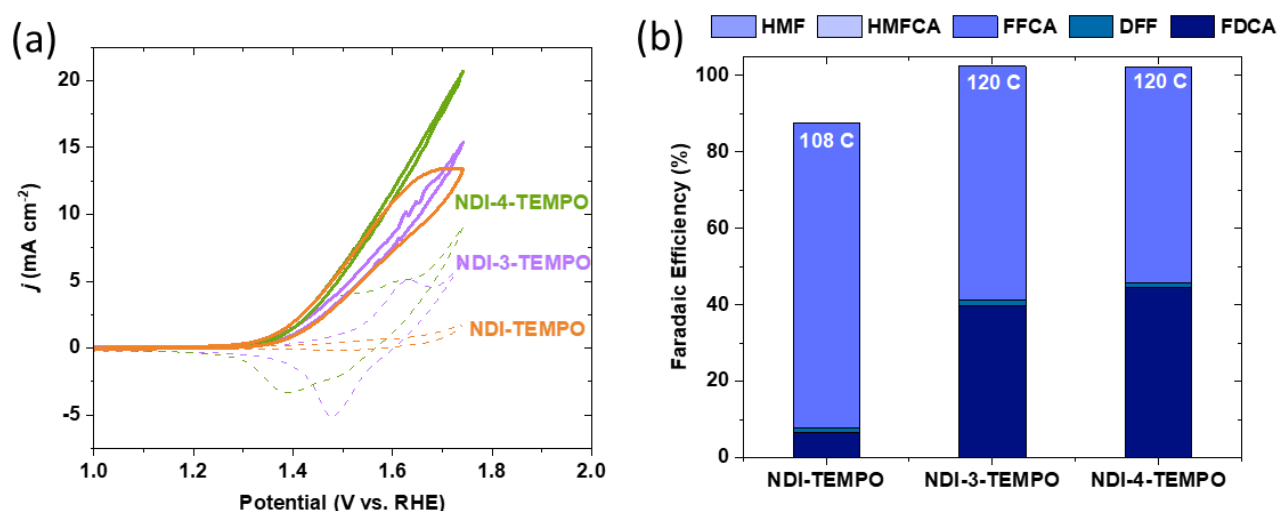


Figure 6.5.1. HMF oxidation activity of NDI-TEMPO, NDI-3-TEMPO, and NDI-4-TEMPO. (a) CVs of said catalysts before (dashed line) and after (solid line) the addition of 10 mM HMF. (b) Faradaic efficiencies of HMF oxidation products on all NDI catalysts. Reaction conditions: 0.1 M potassium bicarbonate-carbonate buffer (pH 10), catalyst loading for CVs was 0.3 mg cm^{-2} with a scan rate of 50 mV s^{-1} , and for constant potential experiments all loading was 2 mg cm^{-2} with chronoamperometry at 1.45 V vs. RHE .

The apparent deactivation of the catalysts was studied further to determine whether the drop in current was purely the result of catalyst degradation. **Figure 6.5.2a** shows the cyclic voltammograms of FFCA as well as the other intermediates of HMF oxidation. Interestingly, the intermediates which contain a carboxyl group show decreased activity for oxidation – even including HMFCa which contains a favourably oxidisable primary alcohol group, compared to DFF and FFCA. FFCA showed almost no oxidation activity compared to the blank CV. The decrease in oxidation activity for carboxyl-containing species is attributed to the electron-withdrawing COOH group that results in the compound being more electron-poor, and hence less likely to be oxidised. This would also be expected for DFF

due to it containing two CHO groups, however, in the alkaline electrolyte, these aldehyde groups are likely nucleophilically hydrated with OH^- which can be further oxidised in the TEMPO catalytic cycle.

Figure 6.5.2b depicts the chronoamperometry of NDI-TEMPO for 10 mM HMF oxidation at 1.45 V vs RHE. It is seen that over 10 hours the current density decreases to almost zero, which we will label as a catalyst ‘deactivation’. Once again, FFCA was the major organic product at this point (~80% FE) and was produced with almost all the supplied electrons being accounted for. To further eliminate major catalyst degradation the reason for this drop in current, a fresh NDI-TEMPO electrode was prepared to continue the oxidation of the same solution, where it was seen that currents were still significantly lower compared to the starting HMF solution and almost matched the current after the prior chronoamperometry measurement. The total loading of both the fresh and initial anode is assumed to be constant, however inaccuracies may arise due to catalysts lost during drop casting of the catalyst, which may affect current densities. Combining this observation and the result from using FFCA as the initial feedstock, a reasonable conclusion can be reached which suggests catalyst degradation is not the major factor for the drop in current density, but instead that the final oxidation step of FFCA $\rightarrow$ FDCA, is very sluggish under these conditions.

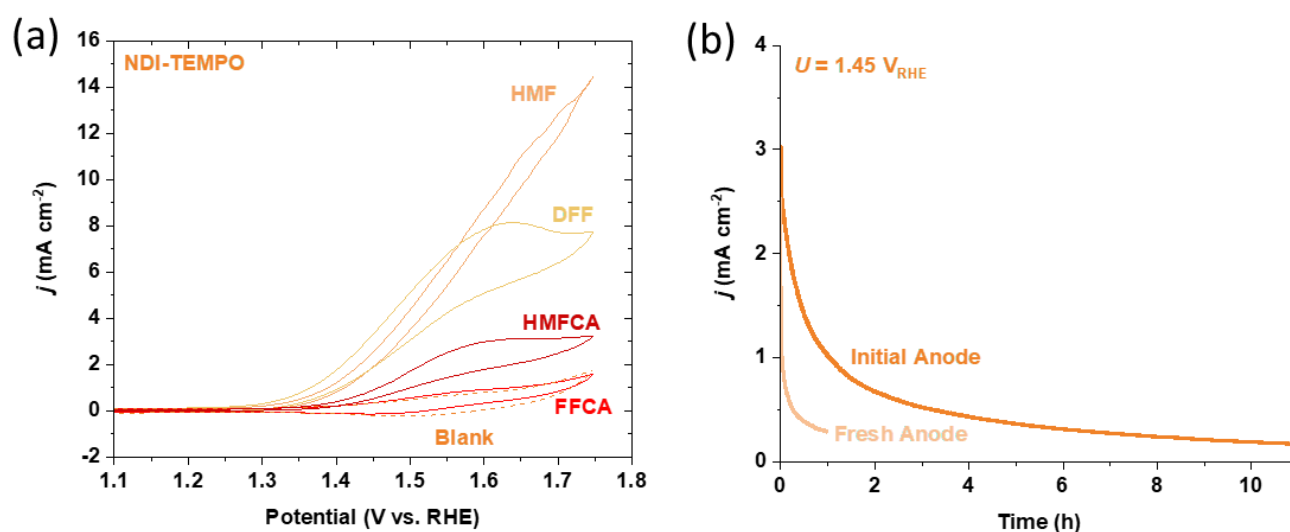


Figure 6.5.2. Electrochemical oxidation activity of HMF and other partial oxidation products on NDI-TEMPO. (a) CVs of NDI-TEMPO before (dashed line) and after (solid lines) the addition of 10 mM HMF, DFF, HMFCa, and FFCA. (b) Chronoamperometry of NDI-TEMPO at 1.45 V vs RHE using 10 mM HMF. A fresh anode with the same loading was used directly after the initial anode was used. Reaction conditions: 0.1 M potassium bicarbonate-carbonate buffer (pH 10), catalyst loading was 0.3 mg cm⁻². The scan rate was 50 mV s⁻¹.

Another interesting property that was observed on all these catalysts was the apparent ability to regenerate catalytic activity after what seemed to be catalyst deactivation, providing there is still some HMF left in the electrolyte after apparent deactivation. **Figure 6.5.3** shows the catalytic activity of a

low loading of 0.3 mg cm^{-2} NDI-TEMPO before and after the addition of 10 mM of HMF, and the following CVs after one hour of constant potential measurements at 1.45 V vs RHE, with the electrode showing almost zero activity (deactivation). Once the electrode was swept in the cathodic direction to -0.80 V vs RHE, a reduction peak was seen, which would disappear on the very next sweep (**Figure C5**). Sweeping anodically again after a cathodic sweep resulted in oxidation currents being almost restored (**Figure 6.5.3**). It is postulated that some of the initial deactivation could be likely a result of catalyst poisoning by an organic species, which can be removed from the catalyst surface during the cathodic sweep, or it could be possible that bubbles from the HER during the sweep could introduce more TEMPO moieties on the surface and remove deactivated ones.

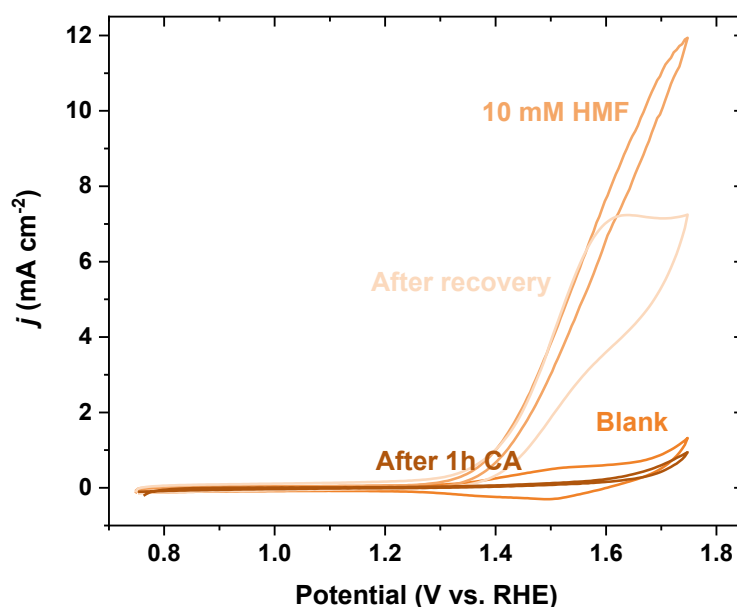


Figure 6.5.3. The recovery ability of NDI-TEMPO after oxidation of 10 mM HMF. The term “after recovery” is defined by a linear sweep from 0.80 to -0.80 V vs RHE in the cathodic direction. Chronoamperometry for 1 h was done at 1.45 V vs RHE. Reaction conditions: 0.1 M potassium bicarbonate-carbonate buffer (pH 10), catalyst loading was 0.3 mg cm^{-2} . The scan rate was 50 mV s^{-1} .

6.6 Effect of Nafion™ Ionomer

Nafion™ ionomer is a perfluorinated sulphonic acid polymer which has properties that make it useful for electrochemical processes.²⁴¹ In this context, Nafion™ was added to prepare catalyst inks and as a binder for carbon-based electrodes which can hold the NDI catalysts in place, to stop the delamination of NDI-TEMPO into the bulk electrolyte. **Figure 6.6.1** shows the CVs of NDI-TEMPO and NDI-4-TEMPO before and after the addition of 10 mM HMF, with and without Nafion™. The blank CVs of NDI-TEMPO show hardly any difference in current densities both with and without Nafion™, whereas NDI-4-TEMPO shows a large decrease in current density on the sample where Nafion™ is used. This result can be attributed to the TEMPO moieties on the sides of NDI-4-TEMPO being free to move without Nafion™, which are otherwise suppressed by the ionomer. The imide-connected TEMPO moieties on both catalysts are out of the plane and may escape this effect. In addition, it may be possible that the Nafion™ disrupts the π - π stacking of these catalysts and can influence the electrical conductivity. For this reason, Nafion™ ionomer was not used in further experiments using NDI-4-TEMPO.

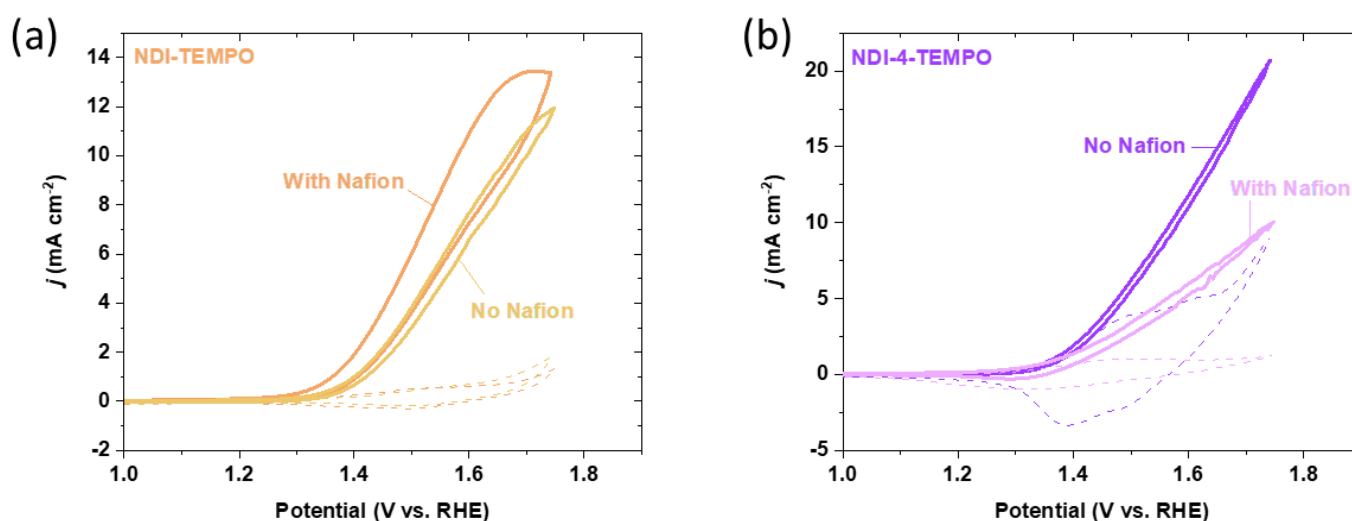


Figure 6.6.1. The effect of Nafion™ ionomer on the oxidation activity of (a) NDI-TEMPO and (b) NDI-4-TEMPO before (dashed line) and after (solid line) the addition of 10 mM HMF. Reaction conditions: 0.1 M potassium bicarbonate-carbonate buffer (pH 10), catalyst loading was 0.3 mg cm⁻², and the scan rate was 50 mV s⁻¹. The amount of Nafion™ added to the ink was calculated at a wt/wt% ratio of 0.5:1 Nafion™ to catalyst.

6.7 Optimisation of NDI-4-TEMPO

NDI-4-TEMPO was chosen as the preferred catalyst to further optimise as it displayed the highest oxidation currents and highest selectivity towards FDCA at low HMF concentrations. For the industrial electrochemical production of FDCA, high current densities and selectivity are required. A higher surface area carbon support of Ketjen Black EC600JD (KB) was explored to help increase current densities further, with the rationale being more surfaces will bear TEMPO moieties that can be in contact with HMF molecules in solution, compared to the lower surface area carbon previously used (VCX-72). **Figure 6.7.1a** shows CVs of 2 mg cm⁻² of NDI-4-TEMPO on 2 mg cm⁻² of KB and VCX-72, before and after the addition of 10 mM HMF. A greater current is observed on KB carbon supports, and from the chronoamperometry measurements (**Figure 6.7.1b**), a larger current was able to be sustained over ten hours.

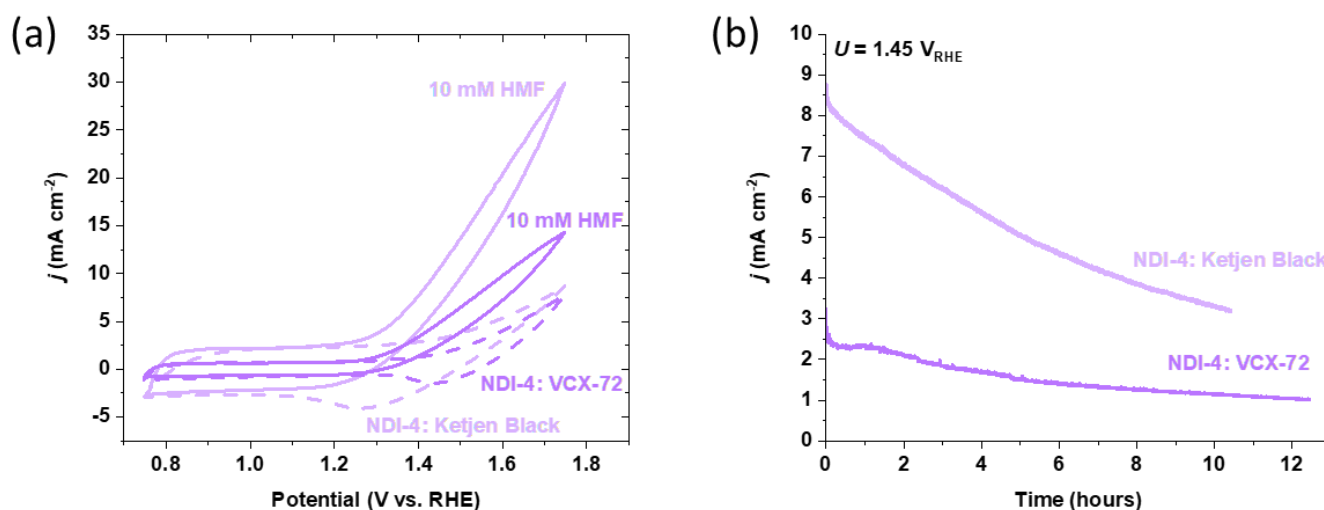


Figure 6.7.1. Electrochemical oxidation activity of NDI-4-TEMPO adsorbed onto different carbon supports. (a) Comparison of CVs of NDI-4-TEMPO before (dashed line) and after (solid line) the addition of 10 mM HMF, on VCX-72 and KB. (b) Chronoamperometries of both carbon supports at 1.45 V vs RHE. Reaction conditions: 0.1 M potassium bicarbonate-carbonate buffer (pH 10), catalyst loading was 2 mg cm⁻². The scan rate was 50 mV s⁻¹.

As KB has a higher surface area, it is also possible to explore a greater wt/wt ratio of NDI-4-TEMPO to carbon, as a greater surface area would be able to accommodate larger concentrations of TEMPO catalysts. Using a 1:1 KB to NDI-4 ratio, we see very similar product selectivities to that of VCX-72, suggesting that the carbon support itself does not alter product selectivity but rather catalyst activity. Different ratios of NDI-4-TEMPO to KB were explored ranging from 0.5:1 to 6:1 (**Figure 6.7.2**). Interestingly, it was observed that lower loadings of 0.5:1, sustained much higher current densities than greater 6:1 ratio. This result was rationalised by the highly hydrophobic NDI-4-TEMPO creating a hydrophobic layer which was blocking access to physisorbed TEMPO from the polar HMF molecules.

In addition, the flat aromatic cores can stack on top of each other making the TEMPO moieties trapped beneath the catalyst layer essentially useless, hence increasing the wt/wt ratio may not be an ideal way of improving activity on these catalysts. The total FE decreases with the higher NDI-4-TEMPO loadings, however, the ratio of detected products remains constant with high amounts of FFCA and relatively low amounts of FDCA (**Figure 6.7.2b**). The increase in unaccounted charge can be explained by some of the electrons being used to destroy some of the NDI-4-TEMPO moieties. We know that an unobstructed route between TEMPO^+ and HMF is required for efficient oxidation, and so a high loading of NDI-4-TEMPO can be detrimental to oxidation activity because some of the active TEMPO^+ species are likely to be located below the electrode surface. This would mean that electrons are able to oxidise TEMPO, but those moieties will not be able to oxidise HMF.

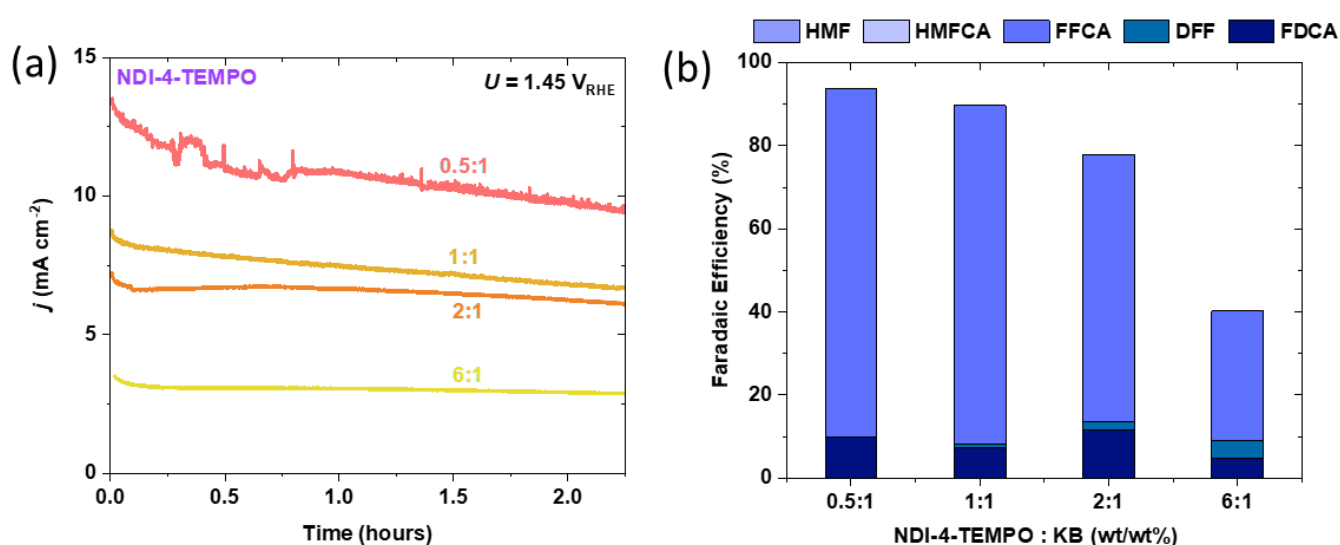


Figure 6.7.2. Optimisation of NDI-4-TEMPO: KB ratio. (a) Chronoamperometries at 1.45 V vs RHE of NDI-4-TEMPO on KB carbon support at different wt/wt loadings. (b) Faradaic efficiencies of HMF oxidation products from each wt/wt ratio. Reaction conditions: 0.1 M potassium bicarbonate-carbonate buffer (pH 10), catalyst loading was 2 mg cm⁻², applied potential was 1.45 V vs RHE for all reactions.

Thus far, low initial HMF concentrations were used during chronoamperometry experiments. The large-scale electrochemical production of FDCA from HMF would require a much larger increase in HMF feedstock, which will naturally result in the increase of current densities due to greater rates of HMF oxidation. **Figure 6.7.3a** shows the CVs of slightly increasing the HMF concentration from 10 to 40 mM, where it was observed that higher concentrations of HMF can gradually increase the current density, but likely reaches a mass transport limitation, likely due to the TEMPO sites being fully saturated on the 1 x 1 cm² electrode used. The chronoamperometry measurements are shown in **Figure 6.7.3b**. Despite a good initial current density of $\sim 10 \text{ mA cm}^{-2}$, the current rapidly falls to $\sim 2 \text{ mA cm}^{-2}$ after 6 h. This is probably due to the oxidation of HMF into FFCA becoming easier as there is a higher concentration of HMF.

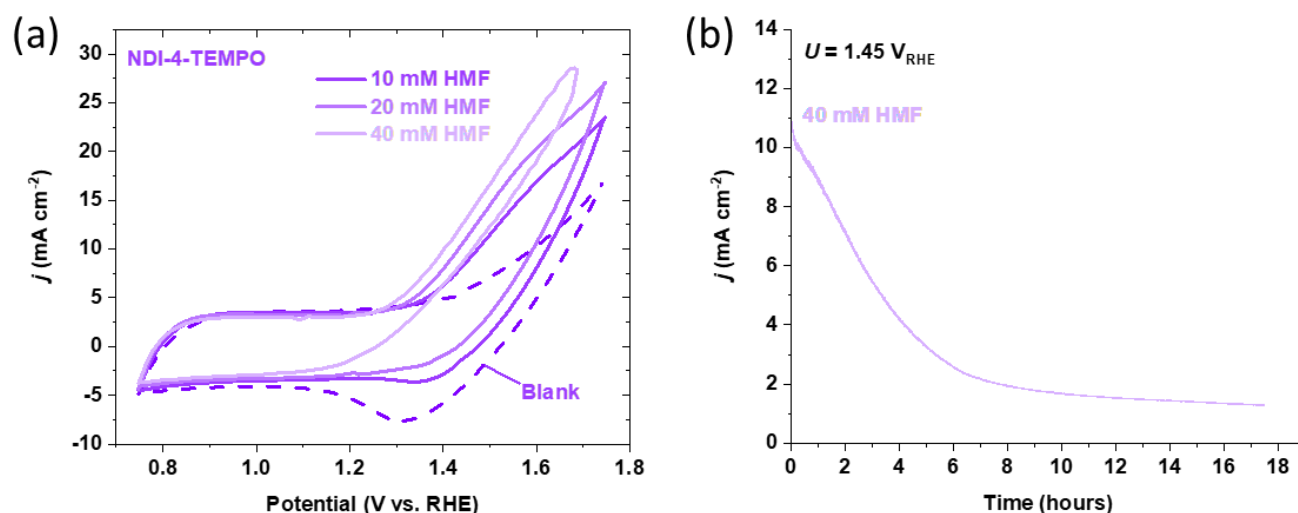


Figure 6.7.3. Electrochemical oxidation of HMF using NDI-4-TEMPO at different initial HMF concentrations. (a) CV of NDI-4-TEMPO before (dashed line) and after (solid line) the addition of different concentrations of HMF. (b) Chronoamperometry of NDI-4-TEMPO at 1.45 V vs RHE using 40 mM HMF. Reaction conditions: 0.1 M potassium bicarbonate-carbonate buffer (pH 10), catalyst loading was 2 mg cm⁻² and was adsorbed onto a KB carbon support. The scan rate was 50 mV s⁻¹.

The effect of OH⁻ concentration was studied by conducting HMF oxidation in a different alkaline pH. It may be possible to promote the sluggish FFCA → FDCA step if sufficient OH⁻ ions can react with the aldehyde to form the active hydrate species. The activity of NDI-4-TEMPO at pH 10 and pH 13 was compared and is depicted in the chronoamperometry in **Figure 6.7.4a**. The experiment in pH 13 produced lower total current densities compared to the reaction at pH 10, and the product profiles reveal a FE higher than 100% in pH 13. This suggests that some FDCA and FFCA is formed through non-electrochemical means, coinciding with the results from the Cannizzaro reaction in **Figure 6.4.1**. From the starting concentration of 10 mM HMF, we were able to account for only about 7.06 mM of the HMF in pH 13, with almost a third of the HMF unaccounted for. This contrasts with the results in pH 10 where we were able to account for almost all the electrons supplied for a 10 mM HMF starting concentration as well as the total FE reaching close to 100%, and most of the 10 mM of HMF is accounted for in the product distribution. The greater loss of HMF at pH 13 is likely due to HMF degradation which is more likely at pH 13, as well as some of the recorded products being produced through non-electrochemical means.

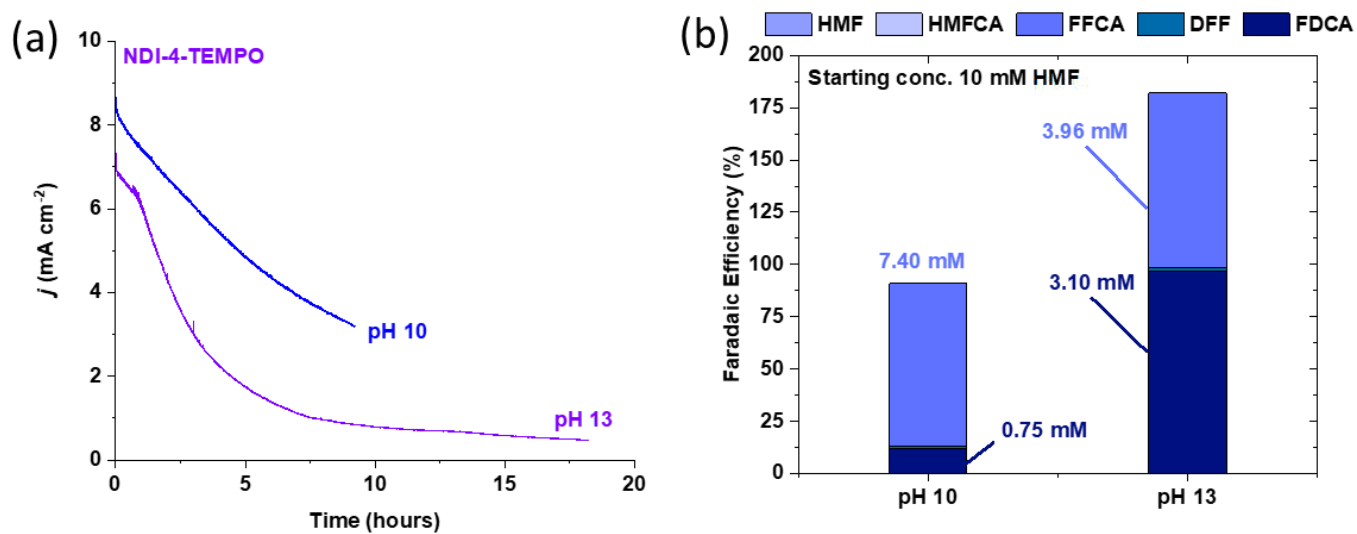


Figure 6.7.4. Electrochemical activity of NDI-4-TEMPO in different alkaline pH electrolytes. (a) Chronoamperometries of NDI-4-TEMPO in pH 10 and 13 starting with 10 mM HMF. (b) Faradaic efficiencies of HMF oxidation products detected after chronoamperometry at 1.45 V vs RHE. Reaction conditions: 0.1 M potassium bicarbonate-carbonate buffer (pH 10), 0.1 M KOH (pH 13), NDI-4-TEMPO catalyst loading was 2 mg cm⁻² and was adsorbed onto KB carbon support.

6.8 Unravelling the Catalyst Regeneration Mechanism

The apparent regeneration of the NDI-TEMPO catalysts after apparent deactivation was an interesting property of these catalysts. XPS was used to probe the N1s, C1s and O1s core levels before, after deactivation and after regeneration of NDI-TEMPO. The N1s core XPS spectra shown in **Figure 6.8.1** suggests that at the deactivation (where the current is almost zero), a new peak appears at ~ 398 eV, which can be attributed to an O-N-O bond coinciding with some poisoning of the active oxoammonium cation after the addition of a nucleophilic species. After regeneration (via an LSV sweep in the cathodic direction) the peak disappears and roughly resembles the spectra of the fresh NDI-TEMPO, although with less intensity likely due to some catalyst delamination. This result suggests that after catalyst poisoning, the LSV sweep either removes the moiety responsible for the poisoning, or the HER bubbles could remove the poisoned species off the surface to reveal new NDI-4-TEMPO surfaces.

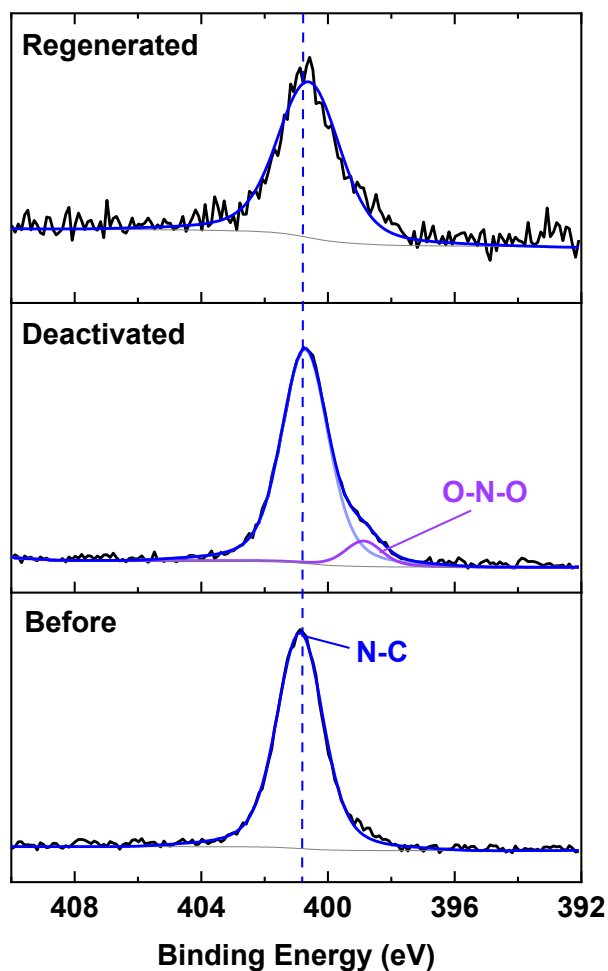


Figure 6.8.1. N1s core level XPS spectra of NDI-TEMPO before, at deactivation, and after recovery of activity after chronoamperometry. Reaction conditions: 0.1 M potassium bicarbonate-carbonate buffer (pH 10), catalyst loading was 2 mg cm^{-2} , 10 mM HMF, potential applied was 1.45 V vs RHE for 1 h. Samples were taken by Yuxiang Zhou and analysed by myself. NafionTM ionomer was not used in this experiment due to machine limitations.

C1s (**Figure C3a**) and O1s (**Figure C3b**) core level spectra were also taken and the O1s spectra shows an increase in intensity at ~533 eV after deactivation. This could be due to the oxidation of the carbon support or perhaps from the poisoning of the radical species by an oxygen containing species. However, after the regeneration from a cathodic sweep, the peak further increases in intensity, which may be a result of more TEMPO moieties get introduced on the surface. The C1s spectra shows no notable change after deactivation, however after regeneration, new peaks appear at ~293 and ~296 eV, as well as a broad peak at ~289 eV. Whilst it is difficult to say what causes the peaks to appear after regeneration, the degradation of the catalyst cannot be ruled out, especially after the O1s spectra revealing some oxidation of the catalyst. In addition, using the NIST database the extra peaks were suggested they may be C-F bonds which could be a result of NafionTM contamination.

6.9 Are There Really Two TEMPO Environments?

It was mentioned earlier in this chapter that the TEMPO moieties on the sides of NDI-4-TEMPO could behave differently to the ones attached using the imide bonds. This property was explored further using *operando* optical spectroscopy, as different oxidation states of TEMPO are known to be UV-active.²⁴² The UV-Vis spectra of all the NDI catalyst explored in this chapter are shown in **Figure C4**. Previous studies were able to use solution UV-Vis spectroscopy to detect TEMPO⁺ and TEMPO⁻ as they are differently coloured. Following this, it is reasonable to hypothesise that UV-Vis spectroscopy can be used to probe the oxidation states of TEMPO on an electrode surface *in situ* using *operando* optical spectroscopy. This technique may be able to detect two separate TEMPO environments on NDI-4-TEMPO which can help explain enhanced oxidation activity of NDI-4-TEMPO compared to NDI-TEMPO.

The CV in **Figure 6.5.1a** shows that NDI-4-TEMPO displays two redox peaks in a blank CV with no HMF, compared to just one redox feature in NDI-TEMPO. This may add credit to the notion that there are two TEMPO environments with different redox properties, which may have different oxidation ability towards HMF and its oxidation intermediates. This may also explain why FDCA was able to be produced in higher quantities on NDI-3 and NDI-4-TEMPO, if the TEMPO moieties on the side chains are more mobile in comparison to the imide connected TEMPO moiety. A reflectance *operando* optical spectroscopy measurement of NDI-4-TEMPO is shown in **Figure 6.9.1** whereby a potential between 1.42 to 1.49 V vs RHE is applied, which coincides with TEMPO oxidation to produce TEMPO⁺. An increase in the wavelengths at 510 and 720 nm is seen as potential increases, and it appears that the first and second redox begin to increase in intensity at slightly different potentials. It is perhaps too early to definitively state that this proves the earlier hypothesis that the two TEMPO environments

act independently and may influence selectivity. Hence, a more detailed study is required to confirm this hypothesis, including probing the spectra after the addition of HMF.

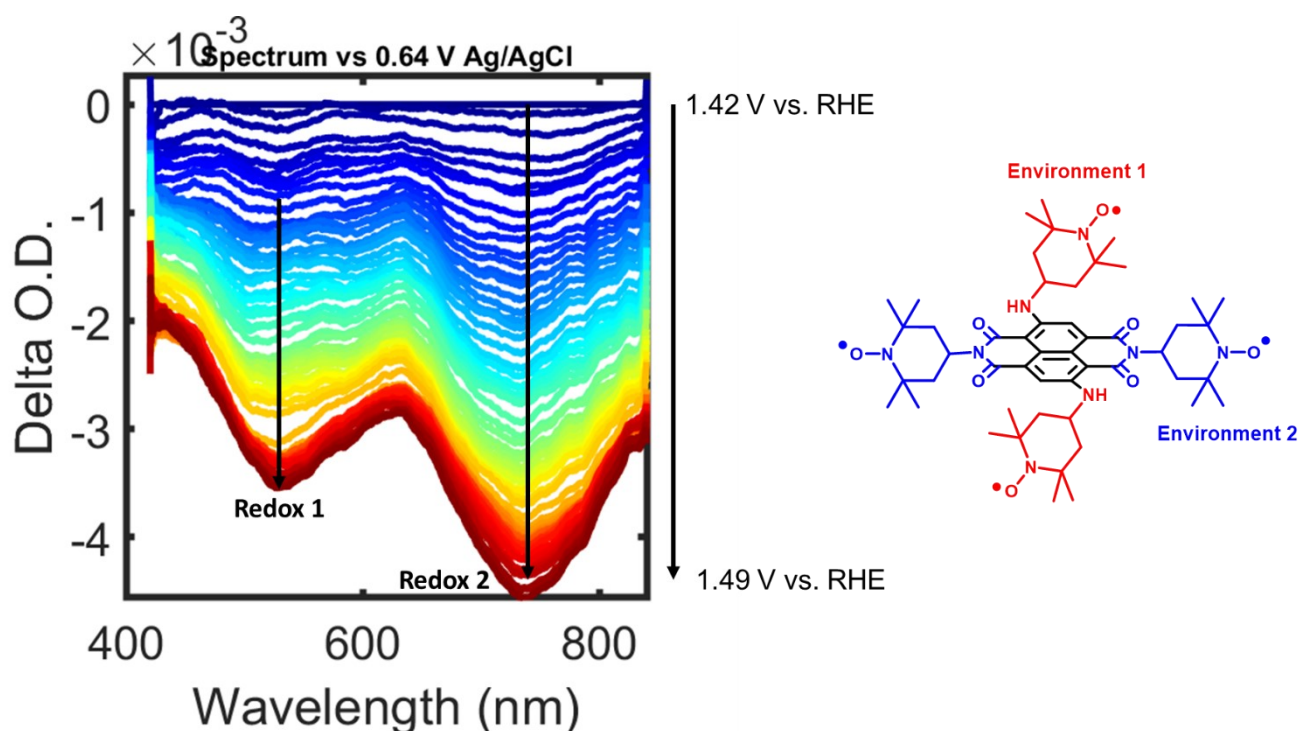


Figure 6.9.1. Reflectance *operando* optical spectroscopy measurements of NDI-4-TEMPO in 0.1 M potassium bicarbonate-carbonate buffer (pH 10). O.D stands for optical density. Measurements done under the supervisions of Caiwu Liang.

6.10 Probing NDI-4-TEMPO Stability with EC-MS

XPS and *operando* optical spectroscopy are not able to give a quantitative explanation of the rate of degradation, instead, electrochemistry-mass spectrometry (EC-MS) was employed for this. The stability of pure NDI-4-TEMPO without any carbon support was tested using EC-MS to probe the degradation of the catalyst in a pH 7 phosphate buffer, with some NafionTM ionomer added to prevent delamination of the catalyst during electrochemistry. No carbon support was used during this experiment to avoid confusing CO₂ evolution from the carbon support with the CO₂ produced from catalyst degradation. CO₂ evolution was quantified at different potentials as it is the most likely product that will be produced during NDI-4-TEMPO degradation. A pH 7 buffer was chosen over a pH 10 bicarbonate solution to avoid any CO₂ coming from bicarbonate ions which could affect the amount of CO₂ produced that is not from catalyst degradation. CO₂ production at potentials between 1.4 V and 1.8 V vs RHE in 100 mV increments was recorded (**Figure 6.10.1**), using a potential hold for 2 minutes at each of potential, then leaving the system to rest for 30 minutes. The rate of degradation

was then able to be calculated, by working out the time needed to degrade all the catalyst from the surface at each potential, quantifying the CO₂ evolved along the duration of the potential holds. It is also worth noting that no oxygen was formed at these potentials.

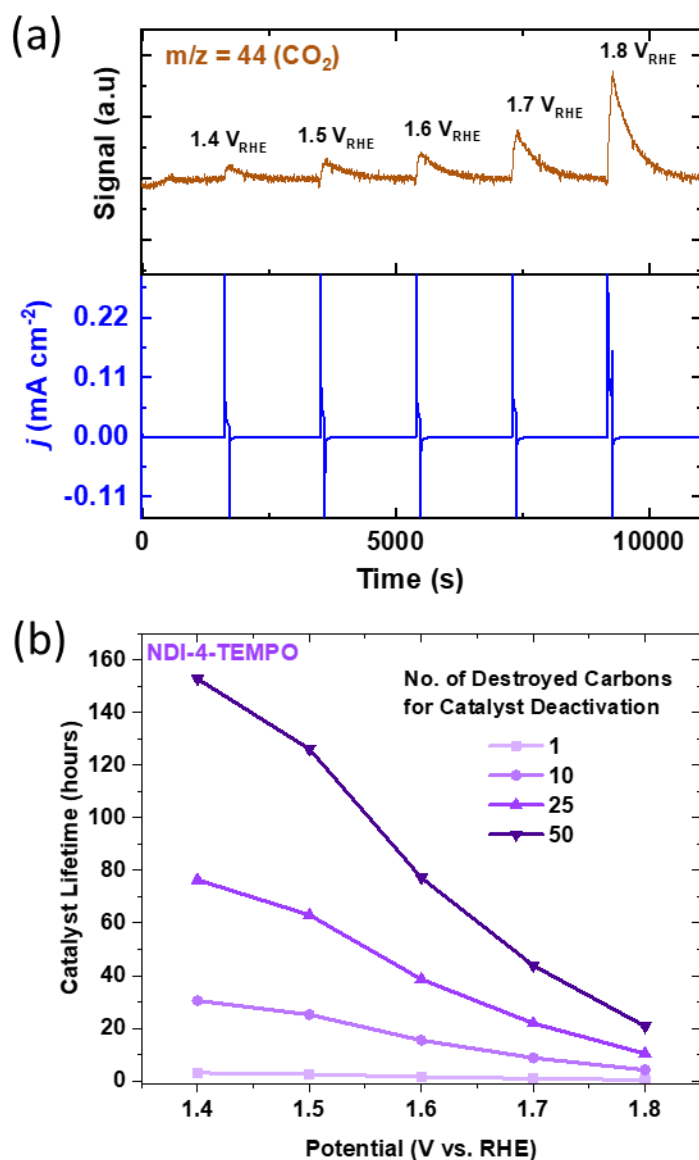


Figure 6.10.1. EC-MS experiments on NDI-4-TEMPO to probe catalyst stability. (a) Mass spectrometry signal of CO₂ produced between 1.40 – 1.80 V vs RHE with current densities. (b) Estimated time required to completely oxidise 0.016 mg of NDI-4-TEMPO. This graph also considers a different number of carbons needed to deactivate the molecules activity. Reaction conditions: 0.1 M potassium phosphate buffer (pH 7), catalyst loading 0.08 mg cm⁻². Measurements were done under the supervision of Yuxiang Zhou.

The destruction of just a few carbons in the catalyst may be enough to render the molecule useless for catalysis, which could happen if degradation occurs at a position where it can affect the activity of the TEMPO radical. To account for this, calculations were done to determine the rate of degradation for a range of different numbers of carbons that could be destroyed. **Figure 6.10.1b** shows the results

of these calculations at different potentials and reports the estimated time needed to degrade the 0.08 mg cm^{-2} of loaded catalyst into CO_2 . At working potentials (1.40 V vs RHE), if just one carbon is enough to destroy complete activity, using the small loadings we used the catalyst should work for about 3 hours, which is extended to 152 hours to completely degrade the 50 carbons that NDI-4-TEMPO has. A moderate estimate of 10 carbons degradation increases the predicted catalyst life to about 30 hours under these conditions which is reasonable, as working conditions should see the time increase due to the higher loadings that will be used. Catalyst lifetime drastically decreases with increasing potential, which is expected because of increased rates of carbon oxidation expected at these potentials, however, potentials above 1.45 V vs RHE will likely not be used for an industrial scale-up.

To help increase catalyst lifetime, a process was developed that aimed to limit the time the catalyst was exposed to such high anodic potentials. As mentioned previously, the oxidation of HMF using TEMPO is indirect once the TEMPO is electrochemically converted to the oxoammonium cation (TEMPO^+). If the current is left on for too long, it could have detrimental impacts on catalyst lifetime. A method was developed to limit this by switching on the current for a short period (60 seconds), followed by a small potential hold at 0 V vs RHE for 5 seconds to simulate switching the current off. This would leave a window where the current is switched off so there is no degradation, meanwhile, HMF oxidation will still occur on the surface TEMPO^+ . An illustration of this is depicted below in **Figure 6.10.2**.

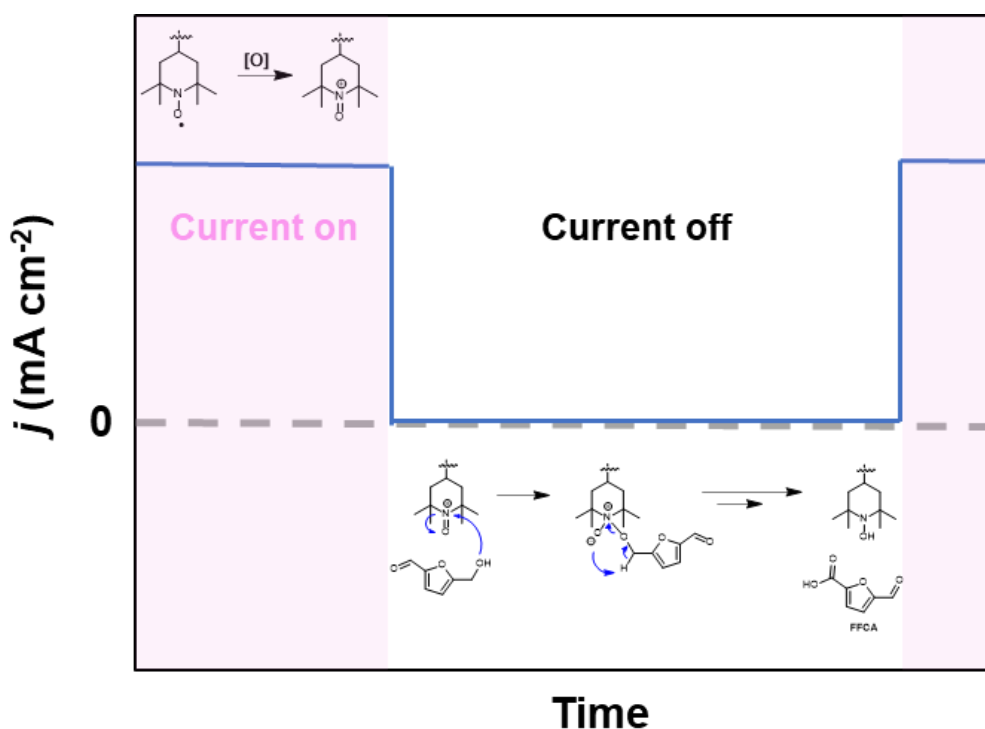


Figure 6.10.2. Illustration of electrochemical oxidation experiment aimed to increase catalyst lifetime by only applying intermittent moments of electricity.

Using this method, a good selectivity towards FFCA was achieved yielding 90% FE, with FDCA as a minor product (8.1%), with an average current density of 2.92 mA cm^{-2} sustained for ten hours. Whilst the total current density was lower than hoped, this still showed promise of increasing catalyst lifetime. An idea for a future study is to optimise this strategy further by extending the time taken at the resting potential, and/or even lowering the resting potential to the recovery redox peak between cycles to help with potential poisoning.

6.11 Continuous FDCA Production

A commercial scale-up attempt was made to produce FDCA and FFCA in an MEA flow cell, like that for reductive amination in the previous chapter. An illustration of the two-electrode setup we used is depicted in **Figure 6.11.1a**. The electrodes consisted of a 2 mg cm^{-2} loading of NDI-4-TEMPO spray coated onto carbon paper as the anode, with Pt mesh used as the cathode as this is the best material for the HER at the counter electrode. The CVs from the MEA before and after the addition of HMF show oxidation activity with good current densities (**Figure 6.11.1b**), and efforts were made to increase currents to industrially relevant levels by increasing the initial concentration of HMF.

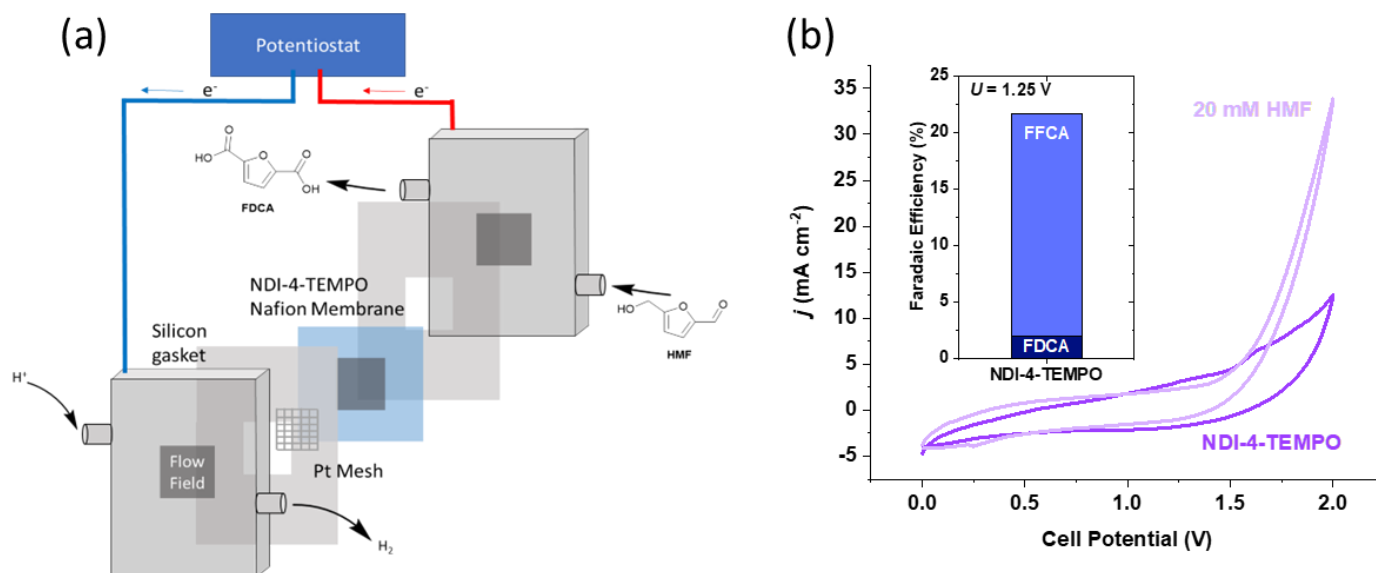


Figure 6.11.1. Continuous electrochemical synthesis of FDCA from HMF using NDI-4-TEMPO. (a) MEA setup of cell used for continuous electrolysis. (b) CVs of NDI-4-TEMPO before and after the addition of 20 mM HMF. Insert graph showing the FE of products obtained from chronoamperometry experiments at 1.25 V. Reaction conditions: 0.1 M potassium bicarbonate-carbonate buffer (pH 10), catalyst loading 2 mg cm^{-2} , the scan rate was 50 mV s^{-1} .

Constant potential experiments were done at a 1.25 V cell potential and revealed a similar product distribution with FFCA being the main product and FDCA as the minor product (**Figure 6.11.1b** inset). However, much less total efficiency was recorded under these conditions. Although the optimisation of the MEA is still in its infancy, it is promising to see that oxidation products were able to be detected under these conditions and will surely be improved following further optimisation.

6.12 Methods for Industrial FDCA Production

Whilst research is still being done aiming to directly produce FDCA from HMF using these catalysts, an alternative way to produce FDCA with good selectivity presents itself from the results already obtained. This begins by using NDI-4-TEMPO to electrochemically oxidise HMF to FFCA and some FDCA in a pH 10 electrolyte to take advantage of the low amount of humins that are produced at this pH, compared to pH 13. FFCA should be formed after this process anywhere between 50-80% of the selectivity, with FDCA forming the final 50-20%. The pH is then raised to pH 13 to increase the rate of the Cannizzaro reaction which will naturally convert the remaining FFCA into FDCA, with some minor amounts of HMFFCA which can equally be oxidised into FFCA which can partake in the cycle again. Finally, a simple pH shift to an acidic pH is required to precipitate out the pure FDCA which is collected. A depiction of this process is illustrated in **Figure 6.12.1**. This process should yield pure FDCA after filtration as the other constituents of the electrolyte are still soluble so will remain in solution.

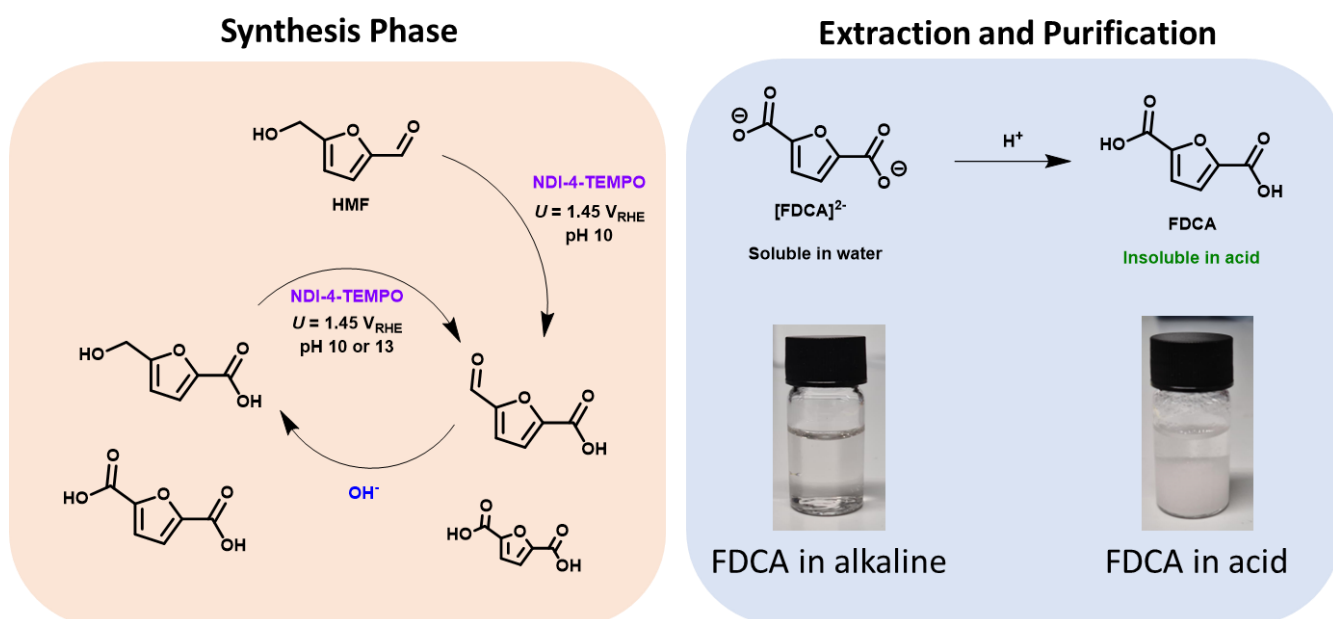


Figure 6.12.1. Synthesis and extraction of FDCA from HMF using NDI-4-TEMPO as an electrocatalyst. The relative size of molecules represents major and minor products.

6.13 Aliphatic Alcohols Oxidation

As an initial exploration away from furanic compounds, the oxidation activity of NDI-4-TEMPO was tested for other platform chemicals sourced from biomass such as ethylene glycol (EG), and glycerol. EG oxidation yields high-value compounds such as glycolic acid, oxalic acid, amongst others.²⁴³ The oxidation activity of NDI-4-TEMPO towards EG oxidation was explored with the resulting CVs before and after the addition of 50 mM EG being shown in **Figure 6.13.1a**. The reaction was done in a pH 13 KOH electrolyte to help deprotonate the OH groups which to make it easier for the alkoxide species to nucleophilically attack the active oxoammonium species. Although an increase in oxidative current is not seen, after the addition of EG to the electrolyte the cathodic peak of the blank NDI-4-TEMPO disappears signalling some form of irreversible oxidation is taking place, which can be attributed to EG oxidation.

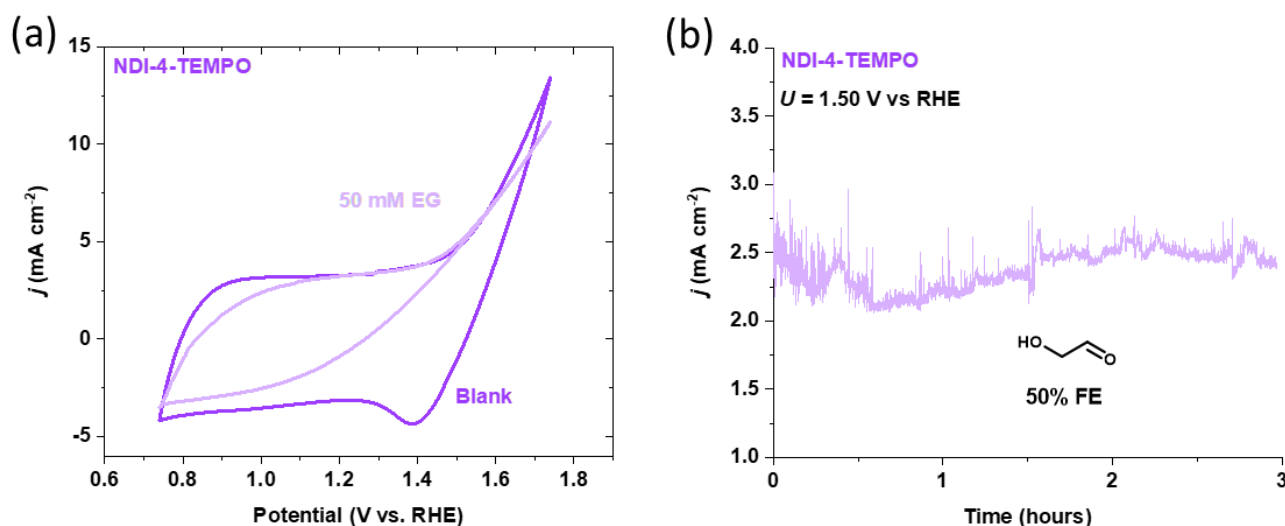


Figure 6.13.1. Electrochemical oxidation of ethylene glycol using NDI-4-TEMPO. (a) LSVs of NDI-4-TEMPO before and after the addition of 50 mM EG. (b) Chronoamperometry of NDI-4-TEMPO at 1.50 V vs RHE. Reaction conditions: 0.1 M KOH (pH 13), catalyst loading 2 mg cm⁻², 50 mM EG. The scan rate for the LSVs was 50 mV s⁻¹.

The total current densities at 1.50 V vs RHE (**Figure 6.13.1b**) for this reaction were around 2.5 mA cm⁻² which is comparatively lower than experiments involving furanic species. 2-hydroxyacetaldehyde (HAC) was produced with 50% FE and was the only detected liquid product after three hours of chronoamperometry, confirming that oxidation activity on NDI-4-TEMPO is not limited to furanic alcohols. In this respect, current densities are comparatively lower, which could suggest that an aromatic ring could help surface adsorption through π - π interactions or by providing extra hydrophobicity which is not present on small chain polyols.

6.14 Conclusion

This chapter explored the electrochemical oxidation of alcohols using immobilised TEMPO electrodes. After confirmation of oxidation activity in a homogenous solution, methods to immobilise TEMPO onto the electrode surface were explored to reap the inherent benefits of heterogeneous catalysis. In this regard, for the first time, the performance of a new group of immobilised TEMPO catalysts using NDI cores used for electrochemical HMF oxidation is reported. Of the analogues that were tested, NDI-4-TEMPO showed the best electrochemical performance for HMF oxidation over the others and was selective towards FFCA with minimal HMF degradation in a mild pH 10 bicarbonate buffer. This offers a great advantage over current state-of-the-art methods which use pH 13/14 electrolytes that catalyses HMF degradation. To the best of our knowledge, this is the first instance of selectively producing FFCA electrochemically. The selectivity was explained by FFCA becoming difficult to oxidise due to electron withdrawing groups making the aldehyde group and furan ring electron poor.

Optimisation of NDI-4-TEMPO activity was achieved by exploring the effects of various parameters including pH, catalyst loading, ionomer effects, initial concentration of HMF, and nature of the carbon support material used. It was concluded that a high surface area carbon support (Ketjen black) was favourable, with a lower catalyst-to-carbon ratio resulting in higher current densities and selectivity. NafionTM ionomer was detrimental to activity possibly due to affecting contact between HMF and TEMPO moieties on the side chains. Although higher concentrations of HMF increased oxidation activity, this must be controlled due to higher rates of humin formation at higher biomass concentrations. EG was also able to be oxidised using NDI-4-TEMPO but with far less activity.

A unique ability to regenerate oxidation activity after what seemed to be catalyst deactivation was probed on these catalysts using XPS. Analysis revealed that the oxidation state of the nitrogen in NDI-4-TEMPO changed when the catalyst was deactivated, but after reactivation following a cathodic sweep, the initial oxidation states of nitrogen were restored, suggesting catalyst poisoning deactivated TEMPO with the removal of the poisoned layer by HER bubbles. Electron paramagnetic studies are underway to probe deeper into the mechanisms behind this property.

The stability of NDI-4-TEMPO was probed using EC-MS, by quantifying the amount of CO₂ evolved at different applied potentials. A reasonable catalyst lifetime was recorded under the working potential of 1.40 V vs RHE, which ranged from 3-152 hours depending on the number of carbons predicted to degrade the catalyst. It is unlikely that carbon supports are stable at the high anodic potentials, so this needs to be addressed perhaps including by using a more robust conductive support.

Lastly, the continuous electrochemical oxidation of HMF was explored using an MEA configuration. Oxidation activity was seen but challenges with efficiency and selectivity on this device were apparent. Optimisation of continuous HMF electrooxidation using NDI-4-TEMPO is underway. A new process was proposed which utilises the Cannizzaro reaction to our benefit whereby the large amounts of FFCA that are produced can be converted into FDCA, by raising the electrolyte pH to 13 to catalyse its production. A simple method to extract the resulting FDCA is proposed by utilising the insolubility of FDCA in an acidic solution.

Appendix C

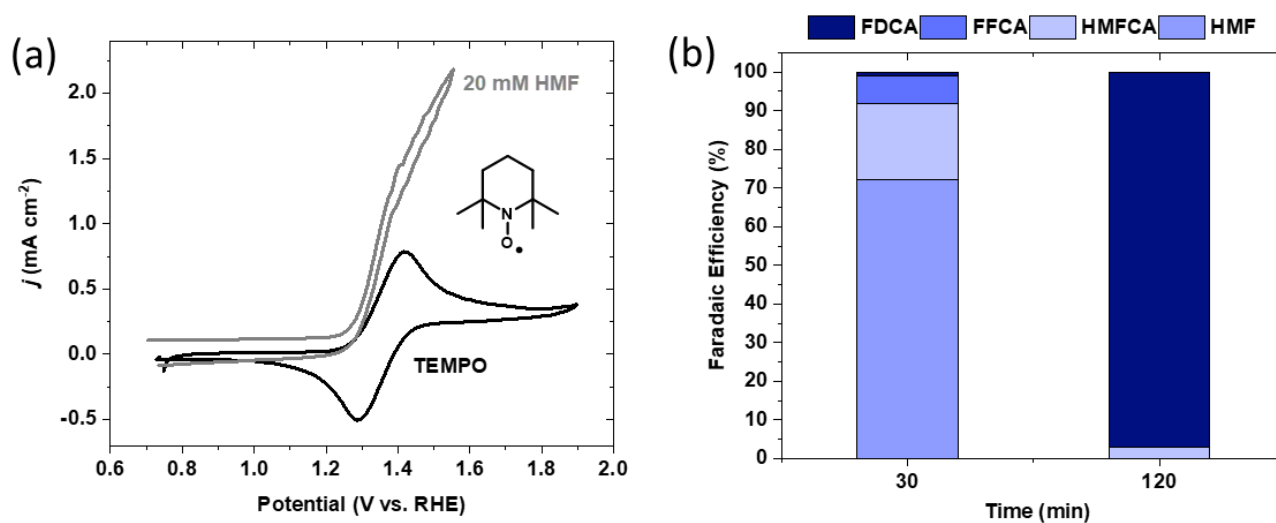


Figure C1. Electrochemical oxidation of HMF using TEMPO. (a) LSVs using carbon electrodes before and after the addition of HMF to a solution of TEMPO. (b) FEs of products detected after 2 h of constant potential experiments at 1.45 V vs RHE. Reaction conditions: 0.1 M potassium bicarbonate-carbonate buffer (pH 10), 4 mM TEMPO, 20 mM HMF, carbon paper electrode. The scan rate was 50 mV s⁻¹.

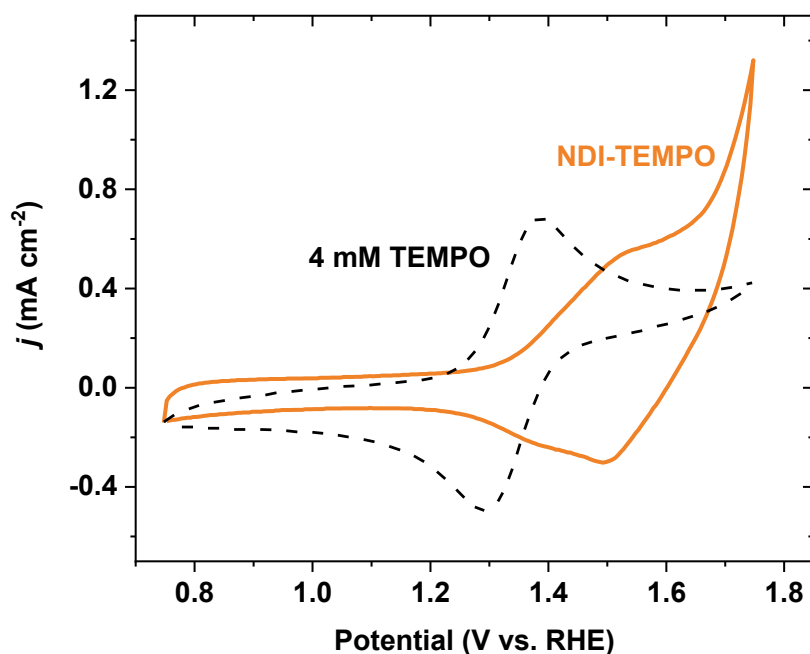


Figure C2. Blank electrolyte LSV of heterogeneous NDI-TEMPO compared to homogeneous the solution of 4 mM TEMPO in pH 10 bicarbonate-carbonate buffer. NDI-TEMPO loading was 0.3 mg cm⁻² on a 1x1 cm² carbon cloth. The scan rate was 50 mV s⁻¹.

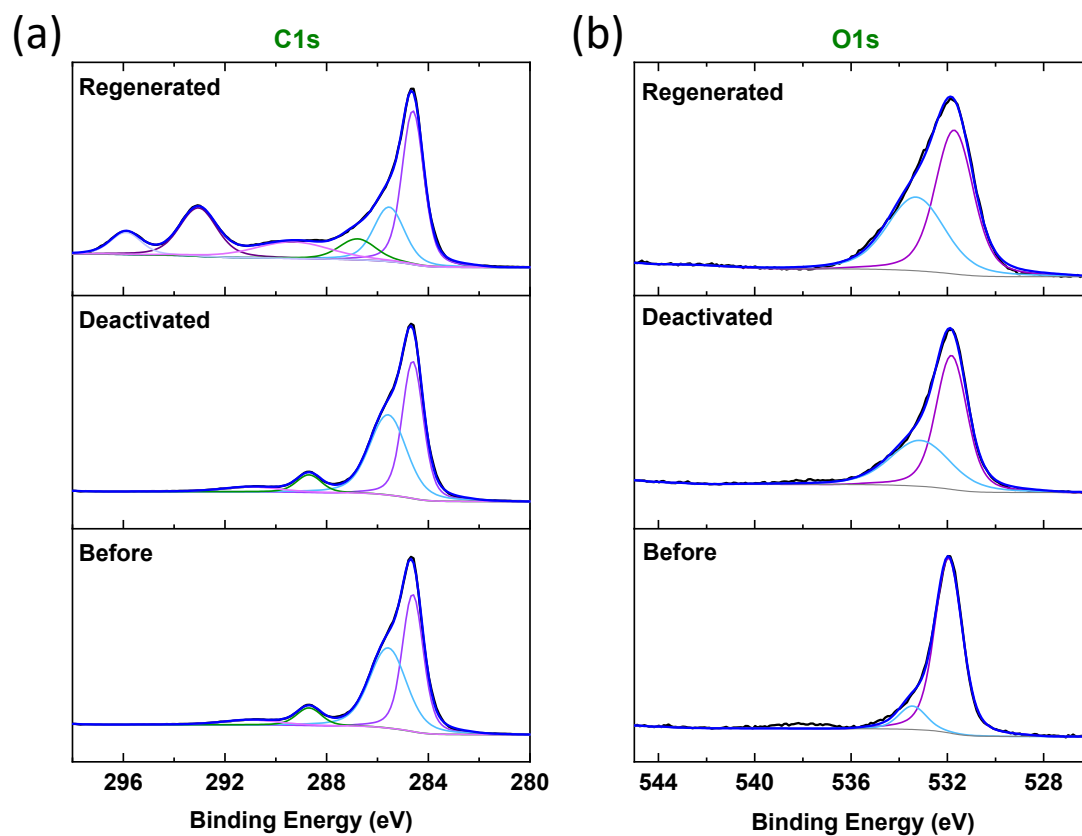


Figure C3. XPS spectra of NDI-4-TEMPO before, during deactivation, and after recovery of activity. (a) C1s and (b) O1s core levels. Reaction conditions: 0.1 M potassium bicarbonate-carbonate buffer, chronoamperometry at 1.45 V vs RHE, catalyst loading was 2 mg cm⁻².

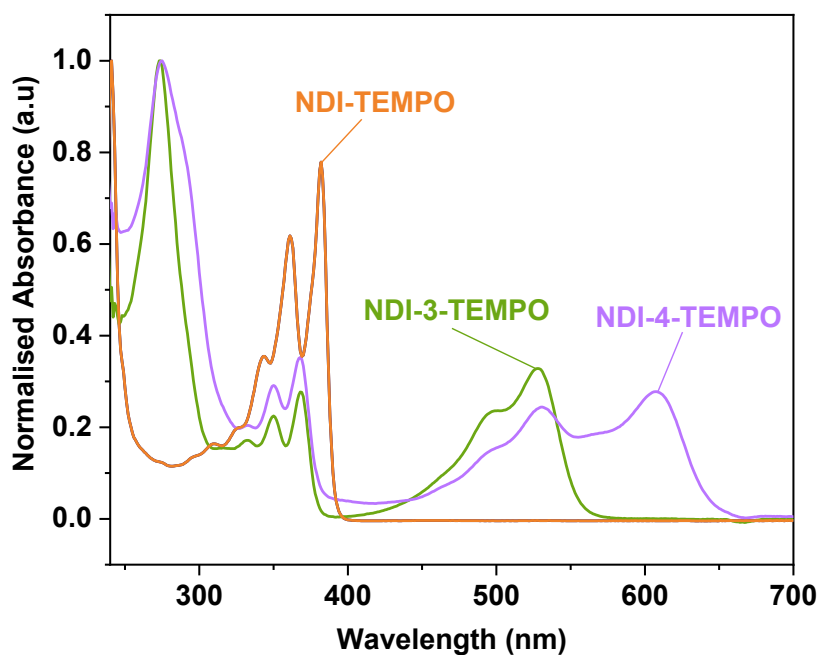


Figure C4. Solution UV-Vis spectra of all NDI catalysts used in this thesis. All samples were dissolved in chloroform.

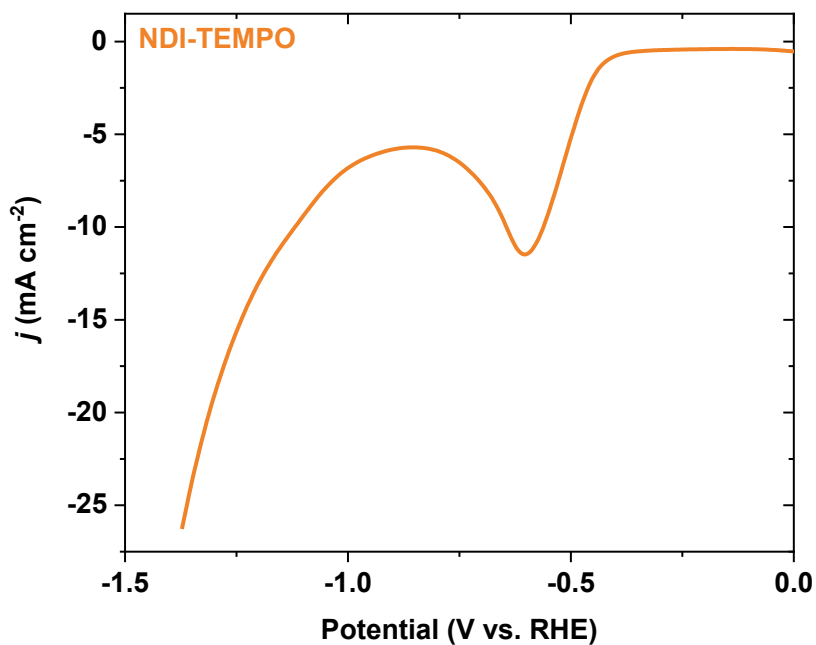


Figure C5. LSV of NDI-TEMPO after deactivation. Deactivation was reached after holding the potential at 1.45 V vs RHE until the current density reached almost zero, and then this LSV was taken. Reaction conditions: 0.1 M potassium bicarbonate-carbonate buffer (pH 10), catalyst loading was 0.3 mg cm^{-2} , 10 mM HMF. The scan rate was 50 mV s^{-1} and was scanned in the cathodic direction.

7 | Summary and Outlook

As the necessary transition away from petrochemical-sourced products begins to take shape, products from lignocellulosic biomass are an effective means to replacing non-renewable petrochemical products and can lower the carbon footprint of many synthesis processes. The primary aim of this thesis was to provide alternative electrochemical synthesis routes to producing new sustainable fuels and chemicals from waste streams which can result in a circular economy, through developing new clean electrochemical technologies which hold realistic possibilities to be commercialised. The limitations, and gaps in understanding of current electrochemical technologies that were detailed in Chapter 2 have been addressed in Chapters 4, 5 and 6 to better help us develop new electrocatalytic processes yielding products for diverse uses.

The intrinsic activity of Cu electrodes was explored in Chapter 4 to elucidate the reduction mechanisms during the production of the high energy density biofuel 2-MF, which have long been disputed in the literature. As Cu is one of the cheapest transition metals, it is reasonable to conclude that Cu cathodes are the best candidates for 2-MF production and merely the other reaction parameters should be optimised for efficient 2-MF electrosynthesis.

The infeasibility for the aviation industry to become fully electrified inspired the need to selectively produce hydrofuroin, which can be used for aviation fuels after further refinement. This further refinement involves ring-opening reactions and will be the focus of future work, to make this process electrified. The selectivity issues of current state-of-the-art electrocatalysts for hydrofuroin synthesis inspired the top-down theory-guided approach of catalyst selection in Chapter 4 as opposed to a more serendipitous approach of testing a range of metals in Chapter 5, for electrochemical reductive amination reactions. As a result of this chapter, a theoretical model now exists that can be used to explore ways to steer the selectivity of furfural reduction products away from purely hydrofuroin. An initial example of this was demonstrated in this chapter whereby single-atom CrTAP catalysts were synthesised following DFT studies, tailored to produce FAL with significantly higher FEs. Although just used for furfural reduction reactions, there is no reason why the same theory cannot be used for the electrovalorisation of other platform chemicals.

Following on from Chapter 4, electrochemical reduction reactions were diversified in Chapter 5 to produce amine derivatives of biomass-derived aldehydes. As the world of electrosynthesis develops, there is growing confidence that the electrochemical nitrogen reduction reaction will be able to one day produce hydroxylamine with good efficiency, which was proven to be an effective source of a possible green nitrogen used to produce amines electrochemically. Ag electrodes displayed the highest FE for this reaction displaying FEs of up to 69% after optimisation, and it was difficult to find a

more efficient electrode than Ag for this reaction. That said, more work is needed to find an Ag material with high enough surface area to produce industrial current densities of over 100 mA cm^{-2} .

Chapter 5 highlighted that an electrosynthesis process is not purely reliant on the catalyst material but other reactions such as intermediate protonation, and nucleophilic addition reactions, that also need to be considered and optimised. The oxidation of HMFA into AFCA using MnO_x electrodes can lower industrial waste produced during multistep syntheses, however, with an FE of only 35% and the poor MnO_x stability, there is room for improvement. From the available literature, and results in Chapter 6, electrochemical alcohol oxidation is much more efficient in alkaline electrolytes, so future work on finding a cathode material able to reductively aminate HMF in alkaline pH is an interesting gap in current literature. This could even tie in with the NDI-4-TEMPO catalysts in Chapter 6. Future work entails optimising the MEA for reductive amination reactions as FEs were relatively low.

Arguably the most valuable results reported in this thesis were the ones described in Chapter 6, detailing immobilising TEMPO onto the electrode surface to electrochemically produce FDCA from HMF. The global demand for FDCA is predicted to skyrocket due to the superior properties of PEF plastics compared to petrochemical sourced PET. This chapter further highlighted that a combination of side reactions can work in unison to the main electrochemical reaction. In this regard, the oxidation of HMF using TEMPO proceeded via an indirect route after oxidation of TEMPO moieties into TEMPO^+ on the electrode surface. The Cannizzaro reaction can also convert FFCA into FDCA which is difficult to achieve electrochemically. The new catalysts and processes to produce FDCA that are reported here have great commercial potential and can be significant in the field of sustainable FDCA production. Work is still needed to optimise a continuous process for FDCA production and improve catalyst lifetime. This is currently being actively pursued by finding supporting materials for NDI-4-TEMPO that are more stable at high anodic potentials. A short summary of the main achievements of the work undertaken in this thesis is depicted in **Figure 7.1**.

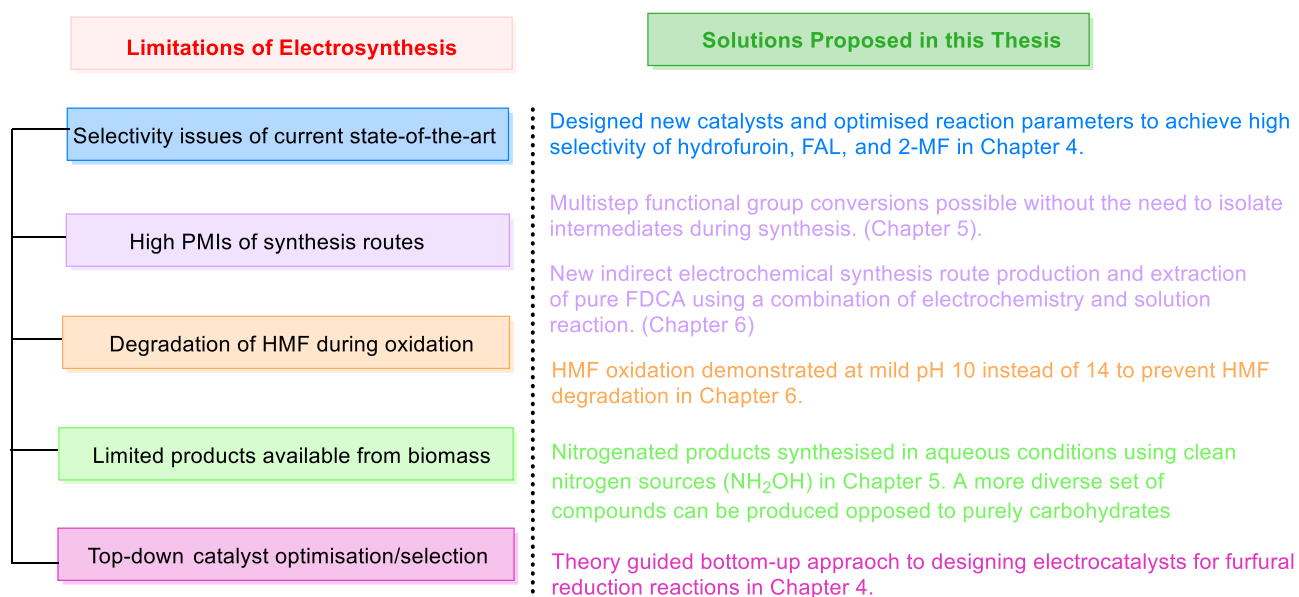


Figure 7.1. Overview of the current limitations for biomass electrovalorisation and the methods of addressing these limitations as studied in this thesis. PMI – process mass intensity.

7.1 Future Adventures – The Electrochemical Biorefinery

The new strategies for biomass electrovalorisation discussed in this thesis have a wide scope for the commercialisation of fuels and fine chemical production via electrochemistry. The themes discussed in this thesis show the potential of utilising biomass as an alternative chemicals source due to the value and diverse purposes of the possible products involved. However, the main challenges currently lie in the scale-up of the reported electrochemical conversions which have efficiency problems and the initial cost of scale-ups. For this to become feasible, the financial incentives must be appealing which require scientists to target products with the highest demand. In this respect, FDCA is a good starting point for a commercial scale-up, but a full life cycle assessment with detailed techno-economic analysis for this project should be undertaken. In addition, whilst efficient routes for hydrofuroin electrosynthesis are reported here, its conversion into straight-chain hydrocarbons for use as jet-fuels needs further consideration. As we are making a fuel, the energy input for this synthesis needs to be accounted for i.e. a considerable net increase in energy output is required. One way this can be overcome is by using green sources of electricity to power the conversions.

The electrosynthesis processes that are described throughout this thesis do not necessarily have to be limited to furanic compounds. An example of this is in Chapter 6 where NDI-4-TEMPO can be used for other small alcohols such as EG to produce glycolic acid. For a realistic possibility to electrify the production of fuels and chemicals, optimisation of parameters is necessary to minimise efficiency loss, and integrate waste streams from other processes that produce useful waste products used as feedstock. To demonstrate commercialisation of the process, a small-scale plant can set up in which we obtain biomass waste, converting it into HMF, then further into FDCA. To the best of our knowledge, no plants like this exist today.

The scale-up of the new processes described in this thesis after further optimisation and refinement may aid in making waste biomass valorisation a genuine contender for a sustainable chemicals source. However, further work still needs to be done to evaluate the costs involved. Although the green benefits are undoubtedly attractive, for the large-scale commercialisation of an electrochemical biorefinery to move a step closer, the financial incentives also need to be attractive, which leads focus into minimising efficiency losses and costs associated with scaling a natural next step.

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Publication: ACS Catalysis
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Publication: ACS Catalysis
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Title Electrochemical Oxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid (FDCA) in Acidic Media Enabling Spontaneous FDCA Separation

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Author Stephen R. Kubota, Kyoung-Shin Choi

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Article Title	Electrocatalytic oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid on supported Au and Pd bimetallic nanoparticles	Publication Type	Journal
Author/Editor	Royal Society of Chemistry (Great Britain)	Start Page	3778
Date	01/01/1999	End Page	3786
Language	English	Issue	8
Country	United Kingdom of Great Britain and Northern Ireland	Volume	16

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Author/Editor	Royal Society of Chemistry (Great Britain)	Start Page	1798
Date	01/01/2010	End Page	1806
Language	English	Issue	7
Country	United Kingdom of Great Britain and Northern Ireland	Volume	11

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TEMPO-Modified Linear Poly(ethylenimine) for Immobilization-Enhanced Electrocatalytic Oxidation of Alcohols
 Author: David P. Hickey, Ross D. Milton, Dayi Chen, et al
 Publication: ACS Catalysis
 Publisher: American Chemical Society
 Date: Sep 1, 2015
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Article Title	Electrochemical reductive amination of furfural-based biomass intermediates	Publication Type	Journal
Author/Editor	Royal Society of Chemistry (Great Britain)	Start Page	5412
Date	01/01/1999	End Page	5417
Language	English	Issue	20
Country	United Kingdom of Great Britain and Northern Ireland	Volume	18

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Article Title	Reviving electrocatalytic reductive amination: a sustainable route from biogenic levulinic acid to 1,5-dimethyl-2-pyrrolidone	Publication Type	Journal
Author/Editor	Royal Society of Chemistry (Great Britain)	Start Page	8428
Date	01/01/1999	End Page	8433
Language	English	Issue	21
Country	United Kingdom of Great Britain and Northern Ireland	Volume	23

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Publication Title	Green chemistry : an international journal and green chemistry resource : GC	Rightsholder	Royal Society of Chemistry
Article Title	Electrochemical reductive biomass conversion: direct conversion of 5-hydroxymethylfurfural (HMF) to 2,5-hexanedione (HD) via reductive ring-opening	Publication Type	Journal
Author/Editor	Royal Society of Chemistry (Great Britain)	Start Page	2956
Date	01/01/1999	End Page	2960
Language	English	Issue	10
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