

ELECTROCHEMICAL REDUCTION OF CO₂ ON COPPER DERIVED SURFACES

NUSRAT RASHID



**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI
FEBRUARY 2021**

@Indian Institute of Technology New Delhi, 2021

ELECTROCHEMICAL REDUCTION OF CO₂ ON COPPER DERIVED SURFACES

by

NUSRAT RASHID

Department of Chemistry

Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

FEBRUARY 2021

*To my father, a sun which nourishes me,
my mother, a moon that soothes me,
and
everyone who strives for a better change.*

Certificate

This is to certify that the dissertation entitled "**ELECTROCHEMICAL REDUCTION OF CO₂ ON COPPER DERIVED SURFACES**" being submitted by **Nusrat Rashid** to the Indian Institute of Technology Delhi, for fulfilment of the requirements for the award of **Doctor of Philosophy** in Chemistry is a record of bona-fide research work carried out by her. She has worked under my supervision and has fulfilled the requirements, which to my knowledge, has reached the requisite standard for the submission of the thesis. The results presented in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.

Prof. Pravin P. Ingole

Associate Professor,
Department of Chemistry
Indian Institute of Technology Delhi

Acknowledgements

بسم الله الرحمن الرحيم

In the name of Allah, the most gracious and the most merciful

All praises are due to Allah alone, the Lord who created universe laden with mysteries and filled humans with zeal and passion for unveiling these mysteries for the betterment of human race. It is only due to Almighty's benevolence and mercy, a child from mountains, like me, was able to tame my fervour for science and knowledge through professional guidance. I bow to Him in praise for weaving my life with countless people who moulded and sculpted me into what I am today. From my parents, who raised me with their sweat and love, my teachers who enlightened and encouraged me to dream big, to all my friends, known-unknown, remembered-forgotten, it has been an entangled web of prayers and guidance, and a collective effort of all to polish me as a human and a researcher.

This work would not have been possible without the support, love, discussion of many people who have been a part of my journey. My Ph.D. supervisor, Dr. Pravin Ingole, takes the central stage. I was amongst first students to join him as a research team and the first one to work on CO₂ reduction. His mentorship has umpteen merits, but his willingness to take new challenges and work dedicatedly towards mastering new skills was inspirational and paramount in my development as an independent researcher. His insightful discussion has always yielded solutions to the problems we were handling. His vision includes creating independent researchers and be an icon of change. It was his push and constant belief that helped to keep working through times of sluggish progress or negative results. I am grateful to him; I never felt constrained by experimental costs, conventional wisdom, or freedom to try new things -- which I learnt from him. I owe my heartfelt gratitude to Dr. Mohsin Ahmad Bhat, who has always been ready to help with the critical analysis of my work. His incessant encouragement

and lively talks made this work more enthralling. He was the one who taught me the essential skill for a physical chemist, "equations talk," which had a lasting effect on my understanding of the subject. The quintessential critical analysis of my work by my DRC, Prof. Anil Verma, Prof. Hemant Kashyap, and Prof Siddharth Pandey refined my work to match the high standards pertinent to research in this problem. I have my special thanks to Prof. N. Kurur, his student Upanshu for helping with NMR studies, Mr Karan for helping with initial GC studies, and all HOD of the Chemistry department who worked tirelessly to make our department a hub of scientific excellence. It will not be an exaggeration to extend my heartfelt gratitude to all my teachers since my primary, who believed in me more than myself and continuously encouraged me to recognise the spark and work for it.

Without a fun laboratory atmosphere, Ph.D. would have been exhausting and bland. I am incredibly thankful for my labmates, who made lab a place of solace and helped with idyllic chatter and discussion as per the need. My special thanks to Miss Shwetambhara for her occasional sumptuous food during initial years, Miss Sonia for being tea and coffee partner and the discussions over it, Mr Pintu, Miss Preeti and Miss Sanyukta for being fun colleagues, friends and helpful hands, Dr. Priyanka, Dr. Pavitra, Dr. Shahla, and Dr. Rasmita for guiding and counselling whenever the situation demanded so and my juniors for being ready to help whenever needed. I am also thankful to the people at IIT who helped with some specific problems throughout the journey. My deepest thanks to the IIT administration for setting up CRF and NRF for students, sans which research would not have been possible. All staff at the Himadri hostel, guards, and administration who made my stay at campus comfortable and safe are deservingly acknowledged.

Friends are songs for life. My friend Miss Hina has always been a patient ear for my discomfort or troubles. Our discussion on science, religion, and philosophy has always boosted my morale. Miss Chesfeeda, Miss Tahira, Miss Asmat, Miss Aabida, Miss Waseema, Miss

Gowsia, Miss Anjum, Miss Hafsa, Miss Basima, Miss Nahida Anjum, Miss Nahida Ramzan, Miss Fatima, Miss Kousar, Miss Shagufta, are those coloured threads of my life's tapestry which make it colourful, serene and complete. The love for research and eloquently advocating for STEM makes Dr. Uzma, one of my frequently consulted seniors. She pampered me with gourmet coffees, teas and snacks all the time, which she filled with her voracious encouragement to internalise science and work for it for community betterment. Dr. Ieeba, Dr. Shalaka, Dr. Sanya, Miss Zaynab, Dr Shazia have been a constant inspiration. Dr. Sabeeha has been a warm roommate keeping it cosy for me. My conference buddy, Miss Iqra, needs a special mention for her love, care, and the excitement we shared for science and travel. Miss Aisha and Miss Sufia have been my go-to hostel friends for snacks, tea, and many positive and encouraging conversations. I am incredibly grateful for the daily '*ijtima*' organised by hostel friends to learn and talk more about spirituality, ethics and morality.

My life or Ph.D. would not have been possible, had not my parents broken the jinx of stereotypes, unfortunately, intact in our society. They raised their daughters and sons alike, working hard for equity. My father worked very hard, at times as a labourer, to ensure we get proper education and opportunities, which, despite being an intelligent brain, he was not able to continue. My mother not only showered her love and care on us; she used her craft to fill any gaps that may have remained for our comfortable upbringing. They revolted against the norm, and I was the first woman from my family to join for higher studies hundreds of miles away from home. Their love, care, and belief have always kept me strong in the face of advisories and saved me from succumbing to the harshness of life. I am proud, happy, and thankful for them being in my life. My brother, Mr. Akib, and my sister, Miss Tabassum, are acknowledged for their love and sibling rivalry; they made me understand the beauty of love even when you have differences. My niece, Hoor ul Ain, and nephew, Amaan Ullah, have been a constant source of joy through all these years. Dr. Waseem, my uncle, who lured me to

science, is the best critic of my student life. Since middle school, it is he who triggers my passion for science. Tours through Delhi for food and chatter with him were always refreshing. The love of my grannies stands out for making me feel jolly. All my cousins are genuinely appreciated for their support and planning travel trips whenever I would get a break from work. My whole family has been a constant source of love, respect, and warmth, who never gave up on me when things seemed not working out. In my extended family, special thanks go to my cousin—an occasional mother, full-time friend, and caregiver, Miss Muzzamil and her family for providing me home away from home, nursing me when I was sick, travelling to my hostel with lots of tasty food and goodies, inviting me over and over again, shopping for me when I could not. And with my joyous heart, I feel deeply entitled to the diverse books and their writers whom I read throughout my school and college life for being the quanta of change in my mindset.

Nusrat Rashid

Abstract

Anthropogenic CO₂ emissions from fossil fuel consumption have opened a Pandora's box of climatic and sustainability problems. Reducing CO₂ into fuels and carbon-based compounds on expenditure of intermittent renewable electricity resources (solar, wind) is a promising way to store this energy and close the carbon cycle. Electrochemical CO₂ reduction (ECR) requires highly efficient, robust and selective catalysts to selectively and efficiently convert CO₂ at lower overpotentials into fuels for commercialisation. This thesis begins with studying the role of various physico-chemical properties like morphology, phase, carbonaceous support, synergism between metal and GO support, and electrode fabrication of a copper nanocatalyst in ECR activity, selectivity and stability in acetonitrile electrolyte system into CO. Similar studies were done on Cu/Cu_xO-GO catalysts in aqueous KHCO₃ electrolyte solutions to transform CO₂ selectively into ethylene. An interplay between the electrode/electrolyte influences the mechanism of the ECR, resulting in different products. This was found true in the case of Cu/Cu_xO-GO catalysts also, where ECR in aprotic solvent like acetonitrile yielded CO and availability of reducible protons shifted reaction selectivity towards ethylene.

High electroactive surface area accelerates the ECR activity and kinks, and porous nature causes an increase in local pH around these shapes, which impedes hydrogen evolution reaction (HER). An extensively branched dendritic morphology has these optimum properties. We studied the role of applied potential, ascorbic acid concentration, temperature and time on the morphology of resultant catalyst and optimised the dendritic structure for maximum surface area and secondary branching. A plausible mechanism for the dendritic growth in electrodeposition was also explained. In wet-dimethylsulphoxide (DMSO), the optimised structure produced 33% ethane from CO₂ at -1.5 V (NHE). HER was inhibited on these structures. A shift from production of ethane in wet-DMSO to ethylene (Faradaic efficiency (FE) of 43%), in KHCO₃ was observed which may be due to solvent effects at the interface.

Presence of solvent at inner Helmholtz layer can alter the product profile by controlling the reducible protons available to the electrode surface. Therefore, even if the catalyst structure is same change of solvents can alter the course. The effect of solvent was found more prominent in dendritic or uneven shapes than in simple and spherical shapes.

For methane production (100) facets on smaller rhombohedral copper catalysts are very efficient for ECR. Controlling the surface texture, finesse, and homogeneity by reverse pulse currents, and presence of surface modifying ionic liquids, catalysts converting CO₂ to CH₄ with an efficiency of 67.4% and at partial current density of 38 mA/cm² were prepared. A study of pulse nature and additive presence was done to gain more insights about the catalyst preparation and its activity.

Catalysts having porous and high surface area increase ECR activity, an ability to adsorb CO₂ and simultaneously having an active redox system for electron transfer to CO₂ should lead to higher currents for CO₂ reduction reaction. Copper metal-organic frameworks (CuMOFs) can act both as CO₂ adsorbents as well as redox metal centres for CO₂ reduction, but their electrochemical instability limits their potential use. To surmount this problem, simple groups like NH₂ were used as replacements on free surface -COOH groups on CuMOFs. This simple transformation increased both ECR activity and electrochemical stability of these CuMOFs. HER is suppressed while hydrocarbons were favoured over simple CO.

Overall, this thesis is outlining the implementation of theoretically predicted and empirically realised catalyst properties in a single catalyst system to enhance the ECR activity and selectivity into energy-dense hydrocarbons like ethylene and methane.

सार

जीवाश्म ईंधन की खपत से मानवजनित CO_2 उत्सर्जन ने जलवायु और स्थिरता की समस्याओं के एक पैडोरा बॉक्स को खोल दिया है। आंतरायिक नवीकरणीय बिजली संसाधनों (सौर, पवन) के व्यय पर CO_2 को ईंधन और कार्बन-आधारित यौगिकों में कम करना इस ऊर्जा को संग्रहीत करने और कार्बन चक्र को बंद करने का एक आशाजनक तरीका है। इलेक्ट्रोकेमिकल CO_2 परिवर्तन (ECR) को अत्यधिक कुशल, मजबूत और चयनात्मक उत्प्रेरक की आवश्यकता होती है जो व्यवसायीकरण के लिए CO_2 को कम ओवरपोटेंशियल्स में ईंधन में कुशलतापूर्वक परिवर्तित कर सकें। यह थीसिस विभिन्न भौतिक-रासायनिक गुणों की भूमिका का अध्ययन करने के साथ शुरू होती है जैसे आकृति विज्ञान, चरण, कार्बोनेस समर्थन, धातु और गो समर्थन के बीच तालमेल, और ECR गतिविधि में एक तांबे नैनोकैटलिस्ट के इलेक्ट्रोड निर्माण, सीओ में एसीटोनिट्राइल इलेक्ट्रोलाइट सिस्टम में चयनात्मकता और स्थिरता। CO_2 को एथिलीन में बदलने के लिए जलीय KHCO_3 इलेक्ट्रोलाइट समाधान में $\text{Cu}/\text{Cu}_x\text{O}-\text{GO}$ उत्प्रेरक पर अध्ययन किया गया था। इलेक्ट्रोड / इलेक्ट्रोलाइट के बीच एक परस्पर क्रिया ECR के तंत्र को प्रभावित करती है, जिसके परिणामस्वरूप विभिन्न उत्पाद होते हैं। यह $\text{Cu}/\text{Cu}_x\text{O}-\text{GO}$ उत्प्रेरकों के मामले में भी सच पाया गया, जहां एसीटीऑनिट्राइल जैसे एप्रोटिक विलायक में ECR CO उपजते हैं और रिड्यूसिबल प्रोटॉन की उपलब्धता ने एथिलीन के प्रति प्रतिक्रिया चयनात्मकता को स्थानांतरित कर दिया है।

उच्च इलेक्ट्रोएक्टिव सतह क्षेत्र ECR गतिविधि को तेज करता है और डूब जाता है, और झरझरा प्रकृति इन आकृतियों के आसपास स्थानीय पीएच में वृद्धि का कारण बनती है, जो हाइड्रोजन विकास प्रतिक्रिया (HER) को बाधित करती है। एक व्यापक रूप से शाखाओं में बँधी हुई आकृति विज्ञान में ये इष्टतम गुण हैं। हमने परिणामी उत्प्रेरक की आकृति विज्ञान पर लागू क्षमता, एस्कोर्बिक एसिड सांद्रता, तापमान और समय की भूमिका का अध्ययन किया और अधिकतम सतह क्षेत्र और माध्यमिक शाखा के लिए वृक्ष के समान संरचना को अनुकूलित किया। इलेक्ट्रोडोडेशन में वृक्ष के समान विकास के लिए एक प्रशंसनीय तंत्र भी समझाया गया था। गीले-डाइमिथाइलसल्फोक्साइड (DMSO) में, अनुकूलित संरचना - 1.5 V (NHE) पर CO_2 से 33% इथेन का उत्पादन करती है। इन संरचनाओं पर HER को रोक दिया गया था। KHCO_3 में एथिलीन (फैराडिक दक्षता (FE)) के ओले-डीएमएसओ में इथेन के उत्पादन से शिफ्ट किया गया था, जो इंटरफ़ेस में विलायक प्रभाव के कारण हो सकता है। भीतरी हेल्महोल्ट्ज़ परत में विलायक की उपस्थिति इलेक्ट्रो सतह तक उपलब्ध रेड्यूसबल प्रोटॉन को नियंत्रित करके उत्पाद प्रोफ़ाइल को बदल सकती है। इसलिए, भले ही उत्प्रेरक संरचना सॉल्वेंट्स का एक ही परिवर्तन है पाठ्यक्रम को बदल सकता है। सरल और गोलाकार आकृतियों की तुलना में विलायक का प्रभाव वृक्ष के समान या असमान आकार में अधिक प्रमुख पाया गया।

ECR के लिए मीथेन प्रोडक्शन (100) के लिए छोटे रॉम्बॉइडरल कॉपर उत्प्रेरकों पर पहलू बहुत कुशल हैं। रिवर्स पल्स धाराओं द्वारा सतह की बनावट, चालाकी और समरूपता को नियंत्रित करना, और सतह को संशोधित आयनिक तरल पदार्थों की उपस्थिति, 67.4% की दक्षता के साथ CO_2 को CH_4 में परिवर्तित करने वाले उत्प्रेरक और $38 \text{ m}/\text{cm}^2$ के आंशिक वर्तमान घनत्व पर तैयार किए गए थे। उत्प्रेरक तैयारी और इसकी गतिविधि के बारे में अधिक जानकारी प्राप्त करने के लिए पल्स प्रकृति और योज्य उपस्थिति का अध्ययन किया गया था।

झरझरा और उच्च सतह क्षेत्र वाले उत्प्रेरक ईसीआर गतिविधि को बढ़ाते हैं, CO_2 को विज्ञापित करने की क्षमता और साथ ही साथ CO_2 में इलेक्ट्रॉन हस्तांतरण के लिए सक्रिय रेडॉक्स प्रणाली होने से CO_2 में कमी की प्रतिक्रिया के लिए उच्च धाराओं का नेतृत्व करना चाहिए। कॉपर मेटल-ऑर्गेनिक फ्रेमवर्क (CuMOF) दोनों CO_2 adsorbents के साथ-साथ CO_2 परिवर्तन के लिए redox धातु केंद्रों के रूप में कार्य कर सकते हैं, लेकिन उनकी विद्युत अस्थिरता उनके संभावित उपयोग को सीमित करती है। इस समस्या को दूर करने के लिए, NH_2 जैसे सरल समूहों का उपयोग CuMOFs पर मुक्त सतह $-\text{COOH}$ समूहों पर प्रतिस्थापन के रूप में किया गया था। इस सरल परिवर्तन ने ईसीआर गतिविधि और इन CuMOFs की विद्युत रासायनिक स्थिरता दोनों को बढ़ाया। एचईआर को दबा दिया गया है जबकि हाइड्रोकार्बन को साधारण सीओ से अधिक पसंद किया गया।

कुल मिलाकर, यह थीसिस ईसीआर गतिविधि और एथिलीन और मीथेन जैसे ऊर्जा-घने हाइड्रोकार्बन में चयनात्मकता को बढ़ाने के लिए एक एकल उत्प्रेरक प्रणाली में सैद्धांतिक रूप से अनुमानित और अनुभवजन्य रूप से उत्प्रेरक गुणों के कार्यान्वयन को रेखांकित कर रही है।

Table of Contents

Certificate	I
Acknowledgements	II
Abstract.....	VI
Table of contents.....	VIII
List of figures.....	XIV
List of tables.....	XXIII
Chapter 1: Introduction	1
1.0 Background and motivation	1
1.1 CO ₂ reduction	3
1.2 Methods used for CO ₂ reduction	4
1.2.1 Thermochemical CO ₂ reduction	4
1.2.2 Photochemical CO ₂ reduction	4
1.2.3 Photoelectrochemical CO ₂ reduction	5
1.2.4 Biochemical CO ₂ reduction	5
1.2.5 Electrochemical CO ₂ reduction (ECR)	5
1.3 Challenges in ECR	6
1.3.1 Overpotentials (η)	6
1.3.2 Current Efficiencies	7
1.3.3 Selectivity	8
1.3.4 Stability of catalyst	9
1.3.5 Cells and electrolyzers	9
1.4 Current state of art materials for ECR	11
1.4.1 For formic acid or formate	11
1.4.2 For syngas (CO + H ₂)	12
1.4.3 Copper for hydrocarbons and oxygenates	13
1.4.4 Morphology	15
1.4.5 Size	15
1.4.6 Crystallographic planes	16
1.4.7 Oxide phases	16
1.4.8 Composites of carbonaceous supports.....	17
1.4.9 Copper metal-organic frameworks (CuMOFs)	18
1.5 Electrolytes	19

1.6 Synthesis of the catalysts	20
1.6.1 Electrodeposition	20
1.6.2 Chemical synthesis of copper metal-organic frameworks (CuMOFs)	23
1.7 Determination and quantification of the ECR products	24
1.8 Objectives	26
1.9 Thesis organisation	26
1.10 References	27
 Chapter 2: Experimental methodology	35
2.0 Introduction	35
2.1 Synthesis methodology	37
2.1.1 Electrodeposition	37
2.1.2 One-pot synthesis of CuMOFs	41
2.2 Characterisation of the nano-electrocatalysts	42
2.2.1 Powder X-ray diffraction (pXRD)	42
2.2.2 Fourier transform infrared spectroscopy (FTIR)	43
2.2.3 Field emission scanning electron microscopy (FESEM)	44
2.2.4 Electron dispersive spectroscopy (EDS) and colour maps	45
2.2.5 Transmission electron microscopy (TEM)	45
2.2.6 Raman spectroscopy	47
2.2.7 X-ray photoelectron spectroscopy (XPS)	47
2.3 Electrochemical methodology	49
2.3.1 Electrodes and electrolytes	49
2.3.2 Electrode fabrication	50
2.3.3 Membrane cleaning and activation	50
2.3.4 Electrochemical cell-setup	50
2.3.5 Data recording and handling	53
2.3.6 Linear and cyclic sweep voltammetry	54
2.3.7 Electrochemical impedance spectroscopy (EIS)	56
2.3.8 Electrochemical active surface area (ECSA)	56
2.4 Product determination	57
2.4.1 Faradaic Efficiencies of gaseous products	57
2.4.2 Faradaic Efficiencies of liquid products	59

2.5 Errors	60
2.6 Conclusions	60
2.7 References	61

Chapter 3: Electrochemical reduction of CO₂ on Copper oxide Anchored to Graphene Oxide Microstructures in Acetonitrile..... 62

3.0 Introduction	63
3.1 Experimental Section	65
3.1.1 Materials and Chemicals	65
3.1.2 Synthesis of Cu/Cu _x O.GO nanocomposites	66
3.1.3 Material characterisation	67
3.1.4 Electrochemical measurements	67
3.2 Results and discussion	69
3.2.1 Synthesis of Cu/Cu _x O.GO nanocomposites	69
3.2.2 Characterisation	70
3.2.3 Electrochemical investigations	75
3.2.4 Choice of deposit collector in electrodeposition, Pt rod vs CFP	76
3.2.5 Effect of electrode fabrication method on ECR activity	79
3.2.6 Effect of GO support and the extent of GO reduction	81
3.2.7 Effect of oxide contents in composite	82
3.2.8 ECR over pCu/Cu _x O.GO(Pt _{Rod}) nano-composite	83
3.2.9 Analysis of the reaction products	87
3.3 Conclusions	91
3.4 References	91

Chapter 4: Electrochemical Reduction of CO₂ to Ethylene on Cu/Cu_xO-GO composites in Aqueous Solution..... 96

4.0 Introduction	96
4.1 Experimental	99
4.1.1 Materials	99
4.1.2 Synthesis of Cu/Cu _x O-GO Composites in powder form and thin films	99
4.1.2.1 Powder form	99
4.1.2.2 Thin films	100

4.1.3 Material Characterisation	101
4.2 Electrochemical measurements	101
4.3 Preparation of electrodes	102
4.4 Results and discussion	102
4.5 Conclusions	115
4.6 References	115
Chapter 5: Optimisation of copper dendritic microstructures for electrochemical reduction of CO₂ to C1 and C2 hydrocarbons in KHCO₃ and wet-DMSO.....	121
5.0 Introduction	122
5.1 Materials and chemicals	124
5.2 Synthesis of dendritic Cu NPs	125
5.3 Material characterisation	126
5.4 Electrochemical measurements	127
5.5 Results and discussion	128
5.5.1 Synthesis and Characterisation of dendritic Cu/Cu _x O NPs	129
5.5.2 ECR in wet-DMSO	129
5.5.3 Optimising the additive concentration	129
5.5.4 Optimising the applied voltage	138
5.5.5 Optimising the reaction temperature	141
5.5.6 Optimising the reaction time for the evolution of dendrites	143
5.5.7 Plausible mechanism of Dendrite formation	147
5.5.8 ECR in 0.2M KHCO ₃	152
5.5.9 ECR on Cu-microstructure Prepared with Varying AsH Concentration	155
5.5.10 ECR on Cu-microstructure electrodeposited with different applied voltages...	158
5.5.11 ECR on Cu-microstructure electrodeposited at varying bath temperatures.....	161
5.5.12 ECR over Cu-microstructure prepared with varying electrodeposition times..	163
5.5.13 Comparative mechanistic aspects of ECR in DMSO and aqueous medium.....	165

5.5.14 Effect of catalyst morphology	167
5.5.15 Effect of crystalline features of a catalyst	168
5.5.16 Effect of solvent; aqueous versus wet organic	179
5.6 Conclusions	172
5.7 References	172

Chapter 6: Reverse pulse copper electrodeposits from aqueous solutions of Cu (II) in presence of BMIM Cl: Tuning for highly selective methane catalysts for electrochemical CO₂ reduction..... 179

6.0 Introduction	179
6.1 Experimental	181
6.1.1 Materials and chemicals	181
6.1.2 Synthesis of the copper nanostructures	181
6.1.3 Synthesis of BMIM Cl	183
6.1.4 Material Characterisation	184
6.2 Results and discussion	184
6.2.1 Synthesis of the copper electrodeposits	184
6.2.3 Characterisations	185
6.3 ECR on the copper electrodeposits	191
6.3.1 Products and activity	192
6.3.2 Partial currents and stability	194
6.3.3 Mechanism of methane production	194
6.4 Conclusions	196
6.5 References	197

Chapter 7: Effect of ligand functional groups on the electrocatalytic activity of copper metal centre towards CO₂ in 2D and 3D CuMOFs..... 202

7.0 Introduction	203
7.1 Methodology	203
7.1.1 Materials and chemicals	203

7.1.2 Electrochemical measurements	203
7.1.3 Electrode fabrication	204
7.2 Results and discussion	204
7.2.1 Synthesis of 2D and 3D CuMOFs	204
7.2.2 Post synthetic modification (PSM) of CuMOFs	205
7.2.3 Characterisation	205
7.2.4 Electrochemical reduction of CO ₂ (ECR)	212
7.2.5 Electrochemical impedance spectroscopy (EIS)	214
7.2.6 Product analysis and Faradaic efficiencies	214
7.2.7 EIS at different potentials	218
7.2.8 FESEM and XPS after electrolysis at -0.7 V	220
7.3 Conclusions	223
7.4 References	223
Chapter 8: Conclusions and future outlook.....	229
8.1 Thesis summary	229
8.2 Future directions	230
8.3 References	231
Appendix A.....	232
Appendix B.....	236
Appendix C.....	248
Curriculum Vitae	266

List of Figures

Figure 1.1: current and projected global energy expenditure in OECD and non-OECD unions. Courtesy: international energy outlook, 2019.....	2
Figure 1.2: CO ₂ emissions due to the usage of fossil fuel energy sources, international energy outlook, 2019.....	2
Figure 1.3: Artificial CO ₂ recycling and usage.	4
Figure 1.4: Schematic on the origins of the overpotentials in ECR.	6
Figure 1.5: Schematic of possible two ways of initial electron transfer to CO ₂ , (left panel) electron transfer, and (right panel) proton-coupled electron transfer.....	7
Figure 1.6: Schematic of HER inhibiting the ECR.	7
Figure 1.7: Schematic of products possible in ECR.	8
Figure 1.8: Schematic of the deactivation of catalyst in ECR for longer periods of electrolysis.	9
Figure 1.9: Schematic of the H-cell electrolyser.	10
Figure 1.10: Schematic of the flow cell electrolyser.	10
Figure 1.11: Schematic of the Sabatier principle for generation of different ECR products.	13
Figure 1.12: Schematic of the two-electrode system for electrodeposition of metal NPs.	21
Figure 1.13: Schematic of the three-electrode system for electrodeposition of metal NPs.	22
Figure 1.14: Schematic of the hydrothermal synthesis route used for organic metal frameworks.	24
Figure 2.1: A flow chart for the steps involved in the electrodeposition of copper catalysts from a sacrificial copper metal rod or a copper solution used in different studies in this thesis.	39
Figure 2.2: Schematic of the cell assembly used for the electrodeposition of copper electrocatalysts under potentiostatic conditions in a two-electrode system.....	39
Figure 2.3: A representational electrodeposition methods used to deposit copper catalysts with constant, pulsed, and reverse pulsed currents.....	40
Figure 2.4: Schematic of the cell assembly used for galvanostatic electrodeposition of copper electrocatalysts in a three-electrode system and a pulsed current application....	41

Figure 2.5: Schematic of the synthesis procedure used to prepare CuMOFs and their amide derived variants.	42
Figure 2.6: Schematic of the X-ray diffractometer system.	43
Figure 2.7: Schematic of the FTIR instrument and its working principle.	44
Figure 2.8: Schematic of the FTIR instrument used in this thesis.	44
Figure 2.9: Schematic of the FESEM instrument and its working principle, (right panel) instrument used for the analysis in the current thesis.	45
Figure 2.10: Schematic of the TEM instrument and its working principle.	46
Figure 2.11: Figure of the TEM instrument used for imaging in this thesis.	46
Figure 2.12: Picture of the Raman spectrometer used for imaging in this thesis.....	47
Figure 2.13: Schematic of an XPS working principle.....	48
Figure 2.14: Schematic of the electrochemical cell assembly and the work station used for measurements in this thesis.	51
Figure 2.15: The cell and electrode assembly used for the CO ₂ reduction in aqueous solutions of KHCO ₃	52
Figure 2.16: Schematic of the LSV, (left panel) sweeping of potential between two values with time at a given scan rate, (right panel) current response from a system with application of potential.	55
Figure 2.17: (left panel) potential sweep applied in a CV, and (right panel) resultant current response at applied potentials.	56
Figure 2.18: Schematic of the electrical double layer.	57
Figure 2.19: GC schematic and working principle.	58
Figure 2.20: Representative GC (upper panel) and (lower panel) calibration curves of standard samples of the gases.	59
Figure 2.21: Schematic of an H1 NMR spectrometer.	59
Figure 2.22: (upper panel) representative NMR spectra and (lower panel) calibration curves of standard liquid samples.	60
Figure 3.1: XRD patterns for the samples obtained by electro-deposition at Pt and CFP.	71
Figure 3.2. FESEM images of (a) pCu/Cu _x O(Pt _{Rod}), (b) pCu/Cu _x O-GO(Pt _{Rod}), (c) fCu/Cu _x O(CFP), (d) fCu/Cu _x O-GO(CFP), (e) pCu/Cu _x O@GO(CFP), and (f) fCu/Cu _x O@GO(CFP). The scale bar is 1 μm.	73

Figure 3.3. Raman spectra showing D and G bands for (a) GO, (b) pCu/Cu _x O-GO(Pt _{Rod}), (c) fCu/Cu _x O-GO(CFP), and (d) fCu/Cu _x O@GO(CFP). The ratio of I _D /I _G was calculated from the normalised peak intensity of I _D and I _G	74
Figure 3.4. CVs recorded in CO ₂ saturated ACN showing effect of synthesis substrate (Pt _{Rod} or CFP) in Cu/Cu _x O NPs (left panel) and Cu/Cu _x O.GO composites (right panel).	77
Figure 3.5: CVs recorded over pCu/Cu _x O(Pt _{Rod}), pCu/Cu _x O-GO(Pt _{Rod}) and fCu/Cu _x O-GO(CFP) samples in CO ₂ saturated ACN solution.	78
Figure 3.6. The quadratic relationship between peak potential and an extent of defects in GO with equation, $y = 0.0724x^2 - 0.487x + 1.71$	81
Figure 3.7. (Left panel) Overlay of CV curves recorded on pCu/Cu _x O-GO(Pt _{Rod}) modified CFP in N ₂ purged (black curve) and CO ₂ saturated (red curve) ACN - 0.1 M TBABF ₄ electrolyte medium.	84
Figure 3.8. CVs recorded on pCu/Cu _x O-GO(Pt _{Rod}) modified CFP electrode in CO ₂ -saturated (red curves for first two scans) and N ₂ saturated (black curve) ACN-0.1 M TBABF ₄ solution.	87
Figure 3.9. FE for different gaseous products obtained after an hour long electrolysis of CO ₂ saturated ACN-0.1M TBABF ₄ solution at an overpotential of 20 mV from their respective cathodic peak potentials, (a) pCu/Cu _x O(Pt _{Rod}), (b) pCu/Cu _x O-GO(Pt _{Rod}), (c) fCu/Cu _x O(CFP), (d) fCu/Cu _x O-GO(CFP), (e) GO, (f) pCu/Cu _x O@GO(CFP), and (g) fCu/Cu _x O@GO(CFP).	89
Figure 4.1. FESEM images of different materials used as electrodes for ECR;(a) pCu/Cu _x O,(b) pCu/Cu _x O-GO, (c) fCu/Cu _x O, (d) fCu/Cu _x O-GO, (e) pCu/Cu _x O@GO (physical layer over layer composite), (f) fCu/Cu _x O@GO – film of Cu/Cu _x O electrodeposited on GO layer.	105
Figure 4.2: XPS spectra of the Cu/Cu _x O-GO composites (a) survey spectrum of the materials; and detailed spectra of Cu 2p, (b) pCu/Cu _x O, (c) pCu/Cu _x O-GO, (d) fCu/Cu _x O, (e) fCu/Cu _x O-GO, and (f) fCu/Cu _x O@GO.	107
Figure 4.3: LSV curves in 0.2 M KHCO ₃ electrolyte argon saturated (dashed lines) and CO ₂ saturated (solid lines); (a) pCu/Cu _x O (black traces) and pCu/Cu _x O-GO (red traces), (b) Thin films; fCu/Cu _x O (violet traces) and fCu/Cu _x O-GO (navy trace).....	108
Figure 4.4. Production rates of ECR products on different catalysts in CO ₂ -saturated 0.2 M KHCO ₃ under continuous CO ₂ -purging for an hour. (a) C ₂ H ₄ at -0.985 V vs RHE and (b) CH ₄ , (c) CO, and (d) H ₂ at different applied potentials and, (e) FE of different products ob pCu/Cu _x O-GO.....	110
Figure 5.1: Overlay of pXRD patterns prepared at different concentrations of ascorbic acid (a), and FESEM images of the materials prepared at (b) 25 mM, (c) 75 mM, and (d) 100 mM concentration of ascorbic acid.	130

Figure 5.2. (Left panel) CV polarisation curves (background corrected) for Cu NPs modified GC electrode in CO ₂ saturated DMSO.	131
Figure 5.3: XRD overlay (a) and FESEM images of samples prepared at different applied voltages viz. (b) 7.5 V, (c) circled portion of (b) shown as an enlarged image, and (d) 15 V (e) CV polarisation curves.	140
Figure 5.4: FE SEM images of samples prepared at different reaction temperatures viz. (a) 60°C, (b) 70°C, (c) 90°C V and (d) XRD overlay.	141
Figure 5.5: Background corrected CV (left panel) polarisation curves for GCE modified with the Cu-microstructures in CO ₂ saturated DMSO. (right panel) FE values obtained for different gaseous products at potentials corresponding to -0.5 mA/cm ²	142
Figure 5.6: (a) FESEM images of samples prepared at different electrodeposition time intervals viz. (a) 10, (b) 20, (c) 30, (d) 40, (e) 45, and (f) 60 minutes.	144
Figure 5.7: XRD overlays (Left panel) of Cu NPs prepared at different electrolysis time intervals. (Right panel) Background corrected CV polarisation curves.	146
Figure 5.8: Growth mechanism of temporal evolution of copper from sphere to polygons to dendrimers.	148
Figure 5.9: LSV polarisation curves in 0.1M CuSO ₄ aqueous solution showing a smooth shift of E _{red} of Cu ²⁺ ions with increase in concentration of added ascorbic acid.	150
Figure 5.10: (a) Comparison of LSV polarisation curves for most-active Cu-microstructured catalysts in argon and CO ₂ saturated 0.2 M KHCO ₃ . (b) Nyquist plots, and (c) product distribution with their FEs in CO ₂ saturated 0.2 M KHCO ₃ at different applied potentials. (d) comparative selectivities of the C1 and C2 hydrocarbons in aqueous and DMSO electrolytes for the same catalyst/electrolyte system at different CO ₂ reduction potentials.	154
Figure 5.11. (a) LSV polarisation curves, (b) Nyquist plots at E _{OCP} , and (c) product profile with FE values at -1.0 V vs RHE recorded on dendritic Cu-microstructures (prepared at different AsH concentrations) modified GCE in CO ₂ saturated 0.2 M KHCO ₃ . (d) Selectivities of the C1 and C2 hydrocarbons in aqueous and DMSO electrolytes.	156
Figure 5.12: (a) LSV polarisation curves, (b) Nyquist plots at E _{OCP} , and (c) product profile with FE values at -1.0 V vs RHE recorded on dendritic Cu-microstructures (prepared at different electro-deposition applied biases) modified GCE in CO ₂ saturated 0.2 M KHCO ₃ . (d) Selectivities of the C1 and C2 hydrocarbons in aqueous and DMSO electrolytes.	160
Figure 5.13: (a) LSV polarisation curves, (b) Nyquist plots at E _{OCP} , and (c) product profile with FE values at -1.0 V vs RHE recorded on dendritic Cu-microstructures (prepared at different electrodeposition bath temperatures) modified GCPE in CO ₂	

saturated 0.2 M KHCO ₃ . (d) Selectivities of the C1 and C2 hydrocarbons in aqueous and DMSO electrolytes.	162
Figure 5.14: (a) LSV polarisation curves, (b) Nyquist plots at E _{OCP} , and (c) product profile with FE values at -1.0 V vs RHE recorded on dendritic Cu-microstructures (prepared at different electro-deposition time durations) modified GCPE in CO ₂ saturated 0.2 M KHCO ₃ . (d) Selectivities of the C1 and C2 hydrocarbons in aqueous and DMSO electrolytes.	164
Schematic 6.1: Synthetic route followed for electrodeposition of the Cu nanostructures.	183
Figure 6.2: X-ray diffractograms of the electrodeposits prepared with constant and pulsed currents.	186
Figure 6.3: FESEM images of the samples, (a) CCED_AsH, (b) CCED_AsH_BMIMCl, (c) PED_AsH_BMIMCl, and (d) RPED_AsH_BMIMCl.(scale bar is 100 nm).	187
Figure 6.4 TEM images of the samples, (a) CCED_AsH, (b) CCED_AsH_BMIMCl, (c) PED_AsH_BMIMCl, and (d) RPED_AsH_BMIMCl.	189
Figure 6.5: Size distribution histograms of different electrodeposits prepared.....	189
Figure 6.6: XPS of the samples prepared, (a) survey spectrum, (b) Cu 2p fitted curves, (c) O 1s, and (d) C 1s.	191
Figure 6.7: (a) LSV traces for samples in CO ₂ saturated 0.2M KHCO ₃ solution, and (b) FEs of different ECR products at -0.74V (RHE) on (a) CCED_AsH, (b) CCED_AsH_BMIMCl, (c) PED_AsH_BMIMCl, and (d) RPED_AsH_BMIMCl.....	192
Figure 6.8: FEs of CH ₄ , CO, C ₂ H ₄ and H ₂ on different catalysts at different applied potentials, (a) CCED_AsH, (b) CCED_AsH_BMIMCl, (c) PED_AsH_BMIMCl, and (d) RPED_AsH_BMIMCl. Error bars from three consecutive measurements are also included.	193
Figure 6.9: Plot of total current density, partial current density for methane, and FE of methane at RPED_AsH_BMIMCl catalyst for 120 minutes of operation.	194
Figure 6.10: Mechanism of methane formation on the studied copper electrodeposits.	195
Figure 7.1: XRD diffractograms (a), FTIR (b1), and zoomed in FTIR (b) of acidic- and amide-MOFs.	206
Figure 7.2: FESEM images, EDX spectra, and colour maps of the acidic- and amide-copper MOFs.	208
Figure 7.3: TEM images of CuBDC and CuBDC-Amide MOFs showing 2D structures.	209

Figure 7.4: Detailed XPS spectra of the CuMOFs, (a) Cu 2p, (b) N 1s, (c) O 1s, and (d) C 1s	211
Figure 7.5: LSV polarisation curves of the (left panel) CuBDC and CuBDC-Amide MOFs, (right panel) CuBTC and CuBTC-Amide MOFs in argon and CO ₂ saturated 0.2M KHCO ₃	212
Figure 7.6: BET adsorption and BJH plots curves of the MOFs	212
Figure 7.7: ECSA curves recorded on the acidic- and amide-MOFs.....	213
Figure 7.8: EIS spectra of the CuMOFs at OCP with an inset of the circuit used to fit the data (left panel), and zoomed-in EIS spectra for better elucidation (right panel).....	214
Figure 7.9: (a) total FE for ECR at different potentials, and (b) HER FEs at different potentials for CuMOFs studied.	215
Figure 7.10: FEs of different ECR products at different potentials on CuMOFs, (a) ethylene, (b) ethanol, (c) formic acid, (d) methane, (e) carbon monoxide, and (f) rate of HER on the CuMOFs for long duration of ECR analysis at -0.7V.	217
Figure 7.11: EIS at different potentials(a) CuBDC-Amide, (b) CuBDC, (c) fitted circuit for EIS of CuBDC-Amide (same circuit fits the data at every recorded potential), and (d) two fitted circuits for lower negative potentials and higher overpotentials as observed for CuBDC	219
Figure 7.12: FESEM images of acidic- and amide- MOFs after 4-hour electrolysis.....	221
Figure 7.13: XPS of Cu 2p (a), and N 1s(b) of CuMOFs post-ECR at -0.7 V.....	222
Figure 7.14: Post-electrolysis XRD of acidic and amide-MOFs.....	223
Figure A-1: XPS spectra of (a) pCu/Cu _x O(Pt _{Rod}), (b) pCu/Cu _x O.GO(Pt _{Rod}) (c) Survey scan of pCu/Cu _x O(Pt _{Rod}), and (d) pCu/Cu _x O(Pt _{Rod}).	232
Figure A-2: FESEM image of GO hand painted on carbon fiber paper (CFP). The scale bar is 1 μ m. (right panel) TEM image of Cu/Cu _x O-GO.....	233
Figure A-3: Plots between change in current to scan rates for different materials to calculate capacitance of these materials.	234
Figure A-4: (Left panel) Effect of working electrode fabrication on electrocatalytic activity of Cu _x O-GO nanocomposite. (Right panel) CVs recorded in presence of CO ₂ for Cu/Cu _x O and Cu/Cu _x O-GO.	234
Figure A-5. Effect of extent of reduction of GO on over-potentials as observed via CV scans.	235
Figure A-6. Redox peaks of ferrocene/ferrocenium couple as recorded on Pt QRE (solid lines) and Ag/AgCl (double junction) (dashed scatter) @ 50 mV/s in an	

acetonitrile solution containing 5 mM ferrocene and 100 mM TBABF ₄ as supporting electrolyte.	235
Figure B-1: EIS of Pt and CFP in a 0.2 M TSC solution with or without GO Inset showing the change in the solution resistance. The graphs were fitted with [Rs([RQ]Q)W] circuit.	236
B-2. XRD patterns of Cu/Cu _x O and its composites with GO. (a) overlay of Cu/Cu _x O-GO composites with intense CFP peaks; (b) (a trace) pCu/Cu _x O, and (b trace) pCu/Cu _x O-GO; (c); (c trace) fCu/Cu _x O, (d trace) fCu/Cu _x O-GO, (e) fCu/Cu _x O@GO.	238
Figure B-3. Raman spectra of the composites with D and G bands at 1350 cm ⁻¹ and 1590 cm ⁻¹ , (a) fCu/Cu _x O@GO, (b) GO., (c) pCu/Cu _x O-GO, (d) fCu/Cu _x O-GO and (e) pCu/Cu _x O@GO.	239
Figure B-4: Detailed EDX elemental scans for the Cu/Cu _x O-GO materials	242
Figure B-5: Detailed XPS scan for C 1s in the materials prepared, showing peaks for -C-C-, -C=O and -COOH groups. (a) pCu/Cu _x O, (b) pCu/Cu _x O-GO, (c) fCu/Cu _x O, (d) fCu/Cu _x O-GO, and (e) fCu/Cu _x O@GO.	242
Figure B-6: Detailed XPS scan for O 1s in all of the materials showing peaks for oxide phase and -OH phase. (a) pCu/Cu _x O, (b) pCu/Cu _x O-GO, (c) fCu/Cu _x O, (d) fCu/Cu _x O-GO, and (e) fCu/Cu _x O@GO.	243
Figure B-7: (a) LSV traces of fCu/Cu _x O@GO and pCu/Cu _x O@GO and GO in 0.2 M KHCO ₃ saturated with CO ₂ . (b) Current as a function of scan rate to calculate capacitance of the materials, ▲ pCu/Cu _x O, ► pCu/Cu _x O-GO, ▼ fCu/Cu _x O, ◆ fCu/Cu _x O-GO, ● fCu/Cu _x O@GO, ■ pCu/Cu _x O@GO.	244
Figure B-8: The time-dependent current density and FE curves for the production of ethylene on pCu/Cu _x O-GO at -0.98 V vs RHE over the time span of 100 minutes.....	244
Figure B-9: Nyquist plots recorded in presence and absence of CO ₂ at OCPs (upper panel), and onset potentials (bottom panel). (a) fCu/Cu _x O@GO, (b) fCu/Cu _x O-GO, (c) pCu/Cu _x O, (d) fCu/Cu _x O, (e) pCu/Cu _x O-GO and (f) pCu/Cu _x O@GO.	245
Figure B-10: Equivalent circuit in Argon saturated solution.	246
Figure B-11: Equivalent circuit in CO ₂ saturated solution.	246
Figure B-12: XRD graphs of the catalyst surfaces post-electrolysis at -0.985V, (left panel) (a trace) pCu/Cu _x O, (b trace) pCu/Cu _x O-GO, and (right panel) (c trace) fCu/Cu _x O, (d trace) fCu/Cu _x O-GO, (e trace) fCu/Cu _x O@GO.	247
Figure B-13: morphological transformation of the spent materials. (a) pCu/Cu _x O, (b) pCu/Cu _x O-GO, (c) fCu/Cu _x O, (d) pCu/Cu _x O-GO and (f) fCu/Cu _x O@GO.....	247

Figure C-1: The EDX spectra giving elemental analysis of the samples prepared with three different concentrations of ascorbic acid additives viz. 25 mM, 75 mM, and 100 mM.	249
Figure: C-2: TEM images of the Cu nano-dendrite samples prepared with three different concentrations of ascorbic acid additives, viz. 25 mM (scale 100 nm), 75 mM (scale 500 nm), and 100 mM (from left to right). The scale bar is 100 nm.	249
Figure C-3: Sample gas chromatograms showing, (left panel) retention times in a standard 1% gas mixtures for CO, CH ₄ , C ₂ H ₄ and C ₂ H ₆ and (right panel) gas chromatogram recorded for optimised catalyst @ -1V (NHE).	251
Figure C-4: Pd UPD CVs recorded on different catalyst surfaces. The magnitude of peak current gives roughly the amount of exposed (111) facets.	253
Figure C-5: Chrono-amperometry curve recorded on the GC electrode modified with Cu nano-dendrite prepared at optimised reaction parameters, in DMSO electrolyte solution under continuous purging of CO ₂ at an applied potential of -1.0 V.....	254
Figure C-6: XRD overlay of the samples prepared with 3 different ascorbic acid concentration for electrodeposition. The emergence of oxide peaks in samples signify electrochemical corrosion of the catalyst under high negative potentials.	255
Figure C-7: XPS of the 3 samples prepared at different ascorbic acid concentrations, (a) Survey scan, b,c,d- elemental scan of carbon in 25 mM, 75 mM, 100 mM samples respectively, e,f,g- oxygen elemental scans of 25 mM, 75 mM, 100 mM, respectively. h,i,j- copper elemental scan for 25 mM, 75 mM, 100 mM samples respectively.....	256
Figure C-8: The EDX spectra giving elemental analysis of the samples prepared at three different applied voltages viz. 7.5 V, 15 V and 30 V. All samples are composed of Cu as major element and oxygen sharing low ratio (lower than 13 % atomic percentage).	256
Figure C-9: TEM images of the Cu nano-dendrite samples prepared with three different applied voltages viz. 7.5 V, 15 V and 30 V.	257
Figure: C-10: TEM images of the Cu/Cu ₂ O nano-dendrite samples prepared with four different reaction temperatures viz. 60°C, 70°C, 80°C and 90°C.	257
Figure C-11: The EDX spectra giving elemental analysis of the samples prepared at four different reaction temperatures viz. 60°C, 70°C, 80°C and 90°C.	258
Figure C-12: TEM images of the Cu nano-dendrite samples prepared with six different reaction time intervals viz. 15 min, 30 min, 45 min and 60 min.	258
Figure: C-13: The EDX spectra giving elemental analysis of the samples prepared at six different electrolysis times viz. 15 min., 30 min., 45 min., and 60 min. FE values for gaseous products (ethane, methane and CO) obtained using samples prepared at different reaction time intervals viz. 15, 30, 40, 45, and 60 minutes at potentials corresponding to -0.5 mA/cm ²	259

Figure C-14: Change in ethane production on 60 min (optimised copper dendritic structure) with applied potentials.	260
Figure C-15: An equivalent circuit fitted to the Nyquist plots obtained on different Cu-microstructures in CO ₂ saturated 0.2 M KHCO ₃ at OCP.	260
Figure C-16: An equivalent circuit fitted to the Nyquist plots obtained on different Cu-microstructures in CO ₂ saturated 0.2 M KHCO ₃ at OCP.	261
Figure C-17: A comparison of the trend in variation of FE values for Cu-microstructure catalysts (prepared with varying concentrations of AsH) in DMSO and KHCO ₃ aqueous medium.	261
Figure C-18: A comparison of the trend in variation of FE values for Cu-microstructure catalysts (prepared at varying applied bias) in DMSO and KHCO ₃ aqueous medium.	261
Figure C-19: An equivalent circuit fitted to the Nyquist plots obtained on different Cu-microstructures in CO ₂ saturated 0.2 M KHCO ₃ at OCP.	262
Figure C-20: A comparison of the trend in variation of FE values for Cu-microstructure catalysts (prepared at varying applied bias) in DMSO and KHCO ₃ aqueous medium.	262
Figure C-21: An equivalent circuit fitted to the Nyquist plots obtained on different Cu-microstructures in CO ₂ saturated 0.2 M KHCO ₃ at OCP.	262
Figure C-22: A comparison of the trend in variation of FE values for Cu-microstructure catalysts in DMSO and KHCO ₃ aqueous medium.	263
Figure C-23: An equivalent circuit fitted to the Nyquist plots obtained on different Cu-microstructures in CO ₂ saturated 0.2 M KHCO ₃ at OCP.	263
Figure C-24: A comparison of the trend in variation of FE values for Cu-microstructure catalysts in DMSO and KHCO ₃ aqueous medium.	264

List of Tables

Table 3.1: Summary of crystalline phases (derived from XRD) along with elemental composition, I_D/I_G ratio, and CV peak potentials of samples synthesised via electrochemical dissolution of Cu.	75
Table 3.2: FE_{CO} reported on different catalysts compared to what we report.	90
Table 4.1: Comparison of conventional catalysts used for ECR with our synthesised catalyst performance.....	114
Table 5.1: Comparison of our synthesised catalyst with state-of-the-art materials for ECR.	171
Table 6.1: Table summarising the ratio of Cu(II)/Cu(0), ratios of Cu(100)/(200) XRD peaks, FE of methane on the prepared samples, and the average size of particles as obtained from TEM images.	190
Table 7.1: Ratio of Cu(II)/Cu(I) and total Faradaic efficiency towards CO_2 reduction on the acidic- and amide MOFs.	222
Table B-1: Summary of the physico-chemical parameters obtained from XRD and Raman spectral analysis.	237
Table B-2: XPS peak positions along with ratio of Cu^{2+} to Cu^+	243
Table C-1: lists the various parameters studied and their effect on the crystalline phase, overpotential and Faradaic efficiency on different samples.	248
Table C-2: Different products obtained at different surfaces in 0.2M $KHCO_3$ and DMSO in a CO_2 -saturated solution at -1.0V (RHE) (NHE in DMSO).	250
Table C-3: Comparison of some state of art dendritic materials with our synthesised material for ECR activity.	252