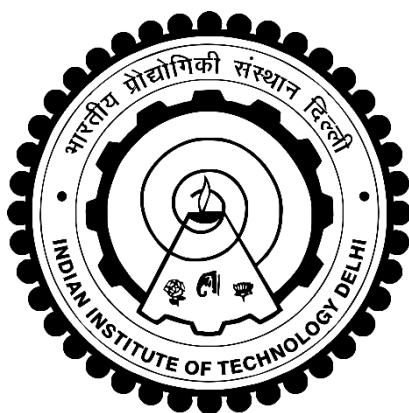


**DEVELOPMENT OF ELECTROSPUN CARBON
NITRIDE-BASED NANOFIBERS AS OXYGEN
REDUCTION CATALYSTS FOR MICROFLUIDIC
FUEL CELLS**

AMANDEEP JINDAL



**DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI
MAY, 2017**

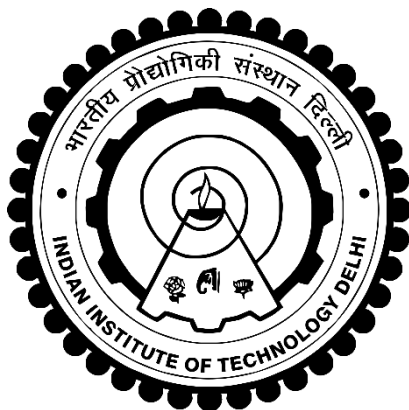
DEVELOPMENT OF ELECTROSPUN CARBON NITRIDE-BASED NANOFIBERS AS OXYGEN REDUCTION CATALYSTS FOR MICROFLUIDIC FUEL CELLS

by

AMANDEEP JINDAL

Department of Chemical Engineering

**Submitted
in fulfilment of the requirements of the degree of Doctor of Philosophy
to the**



**INDIAN INSTITUTE OF TECHNOLOGY DELHI
MAY, 2017**

Dedicated to
my mother, Dr. Anita Rani,
my brother, Arshdeep and his family, Dr. Cosmika and Nitzii

CERTIFICATE

This is to certify that the thesis entitled “**Development of Electrospun Carbon Nitride-Based Nanofibers as Oxygen Reduction Catalysts for Microfluidic Fuel Cells**”, being submitted by **Mr. Amandeep Jindal** to the Indian Institute of Technology Delhi, for fulfilment of the requirements for the award of **Doctor of Philosophy** in Chemical Engineering, Indian Institute of Technology Delhi is a record of bona fide research work carried out by him. He has worked under my guidance and supervision and has fulfilled the requirements, which to my knowledge, has reached the requisite standard for the submission of this thesis. The results contained in this thesis have not been submitted in part or full to any University or Institute for the award of any degree or diploma.

Dr. Suddhasatwa Basu

Professor

Department of Chemical Engineering

Indian Institute of Technology Delhi

New Delhi 110016, India

ACKNOWLEDGEMENTS

I would like to express my deep and sincere gratitude to my guide and mentor, Prof. Suddhasatwa Basu, Department of Chemical Engineering, under whose guidance, inspiration, keen interest and support, I had the opportunity to carry out this study. I shall be indebted to him for believing in me even during the times when my own confidence was low. He always pushed me, encouraged me and understood me which has helped me achieve what I could in my research today.

I wish to thank my committee members, Prof. Ratan Mohan, Dr. Vivek Buwa and Dr. S. Aravindan for their valuable suggestions and requisite guidance on technical issues during my Ph.D. research. I wish to thank Prof. Vikram Kumar for letting me be a part of Nanoscale research facility (NRF), IIT Delhi. I am also grateful to all the faculty members of Chemical Engineering Department and NRF facility for extending their help and cooperation when needed. I utilised the sophisticated characterization and clean room facilities at NRF, IIT Delhi that helped me in my research in a big way. I wish to thank Department of Information Technology (DIT), Government of India for financial support during the execution of research work.

I wish to thank Prof. Sakthi Kumar, Dr. Neha Chauhan, Dr. Tomofumi Ukai, Dr. Aby CP, Dr. Sheikh Mohamed, Dr. Vivekanandan Palaninathan and Prof. Toru Maekawa, Bio-Nano Electronics Research Center, Toyo University, Japan for helping me carry out microfluidic fuel cell research work. I would also like to thank Prof. V. Venkatraman and Mrs. Samudiyatha K.T., Department of Physics, IISc Bangalore for helping me carry out the initial studies in microfluidics. I would like to thank Dr. GVN Rathna, NCL Pune for helping me with the electrospinning technique during my initial Ph.D. days. I would like to thank Prof. A.K. Ganguli for encouraging me and providing me valuable inputs in microfluidics. I would like to thank Mr. Akshey Kaushal for helping me out in carrying out TEM characterization.

I thank all the non-teaching staff of Chemical Engineering Department and NRF for their help and support. It was great pleasure to work in the fuel cell laboratory. I am especially thankful to the young brigade of the fuel cell lab: Mr. Deepak, Ms. Akansha, Mr. Aseem, Mr. Amol, Ms. Garima, Ms. Anu, Ms. Criti, Mr. Debayon, Mr. Arnab for being with me and cheering me up, especially when I was alone. I am also thankful to Dr. Pankaj Kumar Tiwari, Dr. Varagunapandyan N, Mr. Baijnath, Mr. Shahid, Dr. Gurpreet Kaur, Mr. Harikishnan, Dr. Debika Basu, Dr. Rajalekhmi Chockalingam, Mrs. Nitu, Ms. Ieeba, Dr. Kapil, Dr. Merajul, Mr. Ravi and all other lab members. I would like to thank Mr. Sundar Singh for his kind support during the entire period. The support and strength provided by my friends, especially Jasneet Grewal, Sumit, Sanjay, Neeti, Nikhil, Angad, Deepak, Akansha, Simrjit, Deepanshu, Arnab, Harpreet and all other friends was immense. I would like to thank all of them.

When it comes to personal support and strength, I wish to express my heartfelt thanks to my mother, Dr. Anita Rani and my brother, Arshdeep, my sister-in-law, Dr. Cosmika and our cute little Nitzii. Their unflinching support, patience and love have helped me pursue my dreams. My mother, being a professor herself, has always understood me, believed in me and encouraged me at every step to be positive. My brother has always been so helpful and kind to me and without his support, it would not have been possible for me to complete my research work in a timely manner. Lastly, but most importantly, I would like to thank the almighty God for his blessings to give me the strength to put in hard work for my Ph.D. research work.

(Amandeep Jindal)

ABSTRACT

Recent increase in demand of power source for portable devices has increased momentum in research for microfluidic fuel cells (MFC). Electrochemical oxygen reduction reaction (ORR) via non-precious catalysts has the potential for significant cost reduction in commercialization of fuel cells. Towards this end, dense, multi-layered poly(vinyl) alcohol (PVA) nanofibers dispersed with catalytically active carbon nitride (CN_x) nanoparticles are synthesized using electrospinning process. In electrospinning, the polymer solution is passed through high electric field, whereby, electrostatic forces generated stretch the polymer solution into nanofibers, evaporating the solvent. Significant improvement in the electrocatalytic activity of CN_x nanoparticles dispersed in the PVA nanofibers as compared to its native form is observed towards ORR. ORR activity of CN_x is further improved by using polyacrylonitrile (PAN) as a supporting polymer for electrospinning. PAN portrays good spinnability and serves as a secondary source of nitrogen, augmenting the physical and electronic properties of CN_x /PAN nanofibers. In order to disperse CN_x nanoparticles in nanofibrous structure, no high temperature is used in the present work.

ORR activity of CN_x /PAN nanofibers is found to improve further due to addition of fillers, e.g., carbon black and Nafion[®] dispersion (referred to as CN_x nanofibers) and gives comparable ORR activity to that of Pt/C catalyst. While carbon black enhances electronic conductivity, Nafion[®] provides proton conductivity to CN_x nanofibers required for ORR. ORR study for all the catalysts is carried out using linear sweep voltammetry (LSV). SEM, TEM and XPS are carried out to understand the size, morphology and the form of N groups present in the native CN_x nanoparticles and the CN_x /PVA, CN_x /PAN and CN_x nanofibers catalysts. In order to understand ORR mechanism, RRDE and *in-situ* FTIR coupled with cyclic voltammetry (CV) is carried out. RRDE confirms occurring of 4-electron pathway mechanism for ORR and FTIR studies confirms the dominance of ORR in the active potential range by showing the increase

in water formation for the CN_x/PVA , CN_x/PAN and CN_x nanofibers catalysts. The stability of all the nanofiber catalysts towards ORR is confirmed by 5000 repetitions of LSV coupled with FTIR.

MFC with active area of 0.11 cm^2 is fabricated using Y-shape polydimethylsiloxane (PDMS) microchannel, aligned and soft bonded with metallised electrodes. Polarization and power density measurements are carried out for MFC using carbon nitride (CN_x) nanofibers, Pt and Au as cathode catalysts. Formic acid is used as fuel, KMnO_4 as oxidant and H_2SO_4 as supporting electrolyte. MFC flow architecture is optimised such that the diffusion of anolyte and catholyte, which adversely affect the MFC operation at low flow rates is negligible. The maximum power density is achieved at the flow rate of $300 \mu\text{L min}^{-1}$ as compared to flow rate of $400 \mu\text{L min}^{-1}$ and $500 \mu\text{L min}^{-1}$. CN_x nanofibers, as cathode catalyst, exhibit better ability to withstand fuel crossover effect as compared to Pt and Au as it is not active towards formic acid oxidation. Moreover, CN_x nanofibers enable MFC to operate at a wider range of flow rates of fuel and oxidant as compared to Pt and Au. MFC utilising CN_x nanofibers as cathode catalyst exhibits maximum power density of 3.43 mW cm^{-2} and current density of 9.79 mA cm^{-2} , as compared to MFC that utilises Au (2.72 mW cm^{-2} , 6.04 mA cm^{-2}) and Pt (3.09 mW cm^{-2} , 6.18 mA cm^{-2}) as cathode catalyst.

सार

पोर्टेबल उपकरणों के लिए बिजली के स्रोत की मांग में हाल ही में वृद्धि ने माइक्रोफ़्लुइडिक ईंधन कोशिकाओं (एमएफसी) के लिए अनुसंधान में गति बढ़ा दी है। गैर-अनमोल उत्प्रेरक के माध्यम से इलेक्ट्रोकेमिकल ऑक्सीजन रिडक्शन प्रतिक्रिया (ओआरआर) में ईंधन कोशिकाओं के व्यावसायीकरण में महत्वपूर्ण लागत में कमी की संभावना है। इस उद्देश्य के लिए, कार्बन नाइट्राइड (सीएनएक्स) नैनोकणों के साथ फैले हुए घने, बहु-स्तरीय पॉली (विनाइल) अल्कोहल (पीवीए) नैनोफाइबर इलेक्ट्रोस्पिनिंग प्रक्रिया का उपयोग करके संश्लेषित होते हैं। इलेक्ट्रोस्पिनिंग में, बहुलक समाधान उच्च विद्युत क्षेत्र के माध्यम से पारित किया जाता है, जिससे, इलेक्ट्रोस्टैटिक बलों ने विलायक को वाष्पीकरण करने वाले, नैनोफाइबर में बहुलक समाधान को बढ़ाया। सीएनएक्स नैनोकणों के इलेक्ट्रोकेटैलिटिक गतिविधि में महत्वपूर्ण सुधार पीवीए नैनोफाइबर्स में छितराया गया था, क्योंकि इसके मूल रूप की तुलना में ओआरआर की ओर देखा गया है। सीएनएक्स की ओआरआर गतिविधि को इलेक्ट्रोस्पिनिंग के लिए एक समर्थन बहुलक के रूप में पॉलीएक्रिलोनैट्रिल (पैन) का उपयोग करके और बेहतर किया गया है। पैन अच्छा स्पिबिलाबिलिटी दर्शाता है और सीएनएक्स/पैन नैनोफाइबर्स के भौतिक और इलेक्ट्रॉनिक गुणों को बढ़ाकर, नाइट्रोजन का एक माध्यमिक स्रोत के रूप में कार्य करता है। नैनोफाइबर्स संरचना में सीएनएक्स नैनोकणों को फैलाने के लिए, वर्तमान कार्य में कोई उच्च तापमान का उपयोग नहीं किया जाता है।

सीएनएक्स/पैन नैनोफाइबर्स की ओआरआर गतिविधि फिलर के अलावा, कार्बन ब्लैक और नाफियन® के फैलाव (सीएनएक्स नैनोफाइबर्स के रूप में संदर्भित) के अतिरिक्त सुधार करने के लिए और पीटी/सी उत्प्रेरक के बराबर ओआरआर गतिविधि देता है। जबकि कार्बन ब्लैक इलेक्ट्रॉनिक चालकता को बढ़ाता है, नाफियन® ओआरआर के लिए आवश्यक सीएनएक्स नैनोफाइबर्स को प्रोटॉन चालकता प्रदान करता है। सभी उत्प्रेरक के लिए ओआरआर अध्ययन रैखिक स्वीप वोल्टेमेट्री (एलएसवी) का उपयोग किया जाता है। एसईएम, टीईएम और एक्सपीएस को आकार, आकृति विज्ञान और देशी सीएनएक्स नैनोकणों और सीएनएक्स/पीवीए, सीएनएक्स/पैन और सीएनएक्स नैनोफाइबर्स उत्प्रेरक में उपस्थित एन समूहों

के रूप को समझने के लिए किया जाता है। आरआरडीई और इन-सिटू एफटीआईआर को चक्रीय वोल्टैमेट्री (सीवी) के साथ मिलकर समझा जाता है। आरआरडीई पुष्टि करता है कि 4-इलेक्ट्रान मार्ग तंत्र के ओआरआर और एफटीआईआर अध्ययन के लिए सीएनएक्स/पीवीए, सीएनएक्स/पैन और सीएनएक्स नैनोफाइबर्स उत्प्रेरक के लिए पानी के गठन में वृद्धि दिखाकर सक्रिय संभावित सीमा में ओआरआर के प्रभुत्व की पुष्टि करता है। ओआरआर की ओर सभी नैनोफायबर उत्प्रेरक की स्थिरता एफटीआईआर के साथ मिलकर एलएसवी की 5000 दोहरावों द्वारा पुष्टि की गई है।

0.11 सेमी² के सक्रिय क्षेत्र के साथ एमएफसी वाई-आकार पॉलीडिमैथाइलसिलोक्सीन (पीडीएमएस) माइक्रोचैनल, इलेक्ट्रोड के साथ नरम गठबंधन का उपयोग करके निर्मित किया गया। कार्बन नाइट्राइड (सीएनएक्स) नैनोफाइबर्स, प्लैटिनम और सोना का उपयोग कैथोड उत्प्रेरक के रूप में एमएफसी के लिए ध्रुवीकरण और बिजली घनत्व माप को किया जाता है। फॉर्मिक एसिड ईंधन के रूप में इस्तेमाल किया जाता है, केएमएनओ₄ ऑक्सीडेंट और एच₂एसओ₄ के रूप में इलेक्ट्रोलाइट का समर्थन करता है। एमएफसी फ्लो आर्किटेक्चर का अनुकूलन किया गया है, जिससे एनोलाइट और कैथोलाइट का प्रसार, जो कम प्रवाह दर पर प्रतिकूल रूप से एमएफसी ऑपरेशन को प्रभावित करते हैं, नगण्य है। 400 μL मिनिट⁻¹ और 500 μL मिनिट⁻¹ की प्रवाह दर की तुलना में अधिकतम पॉवर घनत्व 300 μL मिनिट⁻¹ की प्रवाह दर पर प्राप्त किया जाता है। कैथोड उत्प्रेरक के रूप में सीएनएक्स नैनोफाइबर्स, पीटी और एयू की तुलना में ईंधन क्रॉसओवर प्रभाव को रोकने की बेहतर क्षमता का प्रदर्शन करते हैं क्योंकि यह फॉर्मिक एसिड ऑक्सीकरण के प्रति सक्रिय नहीं है। इसके अलावा, सीएनएक्स नैनोफाइबर्स एमएफसी को पीटी और एयू की तुलना में ईंधन और ऑक्सीडेंट के प्रवाह दर की व्यापक रेंज पर संचालित करने में सक्षम बनाता है। एमएफसी ने सीएनएक्स नैनोफाइबर्स का उपयोग कैथोड उत्प्रेरक के रूप में 3.43 एमडब्ल्यू सेमी⁻² की अधिकतम पॉवर घनत्व और 9.79 एमए सेमी⁻² की करअंट घनत्व को दर्शाया है, जो एमएफसी की तुलना में एयू (2.72 एमडब्ल्यू सेमी⁻², 6.04 एमए सेमी⁻²) और पीटी (3.09 एमडब्ल्यू सेमी⁻², 6.18 एमए सेमी⁻²) कैथोड उत्प्रेरक के रूप में।

CONTENTS

	Page No.
<i>Certificate</i>	i
<i>Acknowledgements</i>	iii
<i>Abstract</i>	v
<i>Contents</i>	vii
<i>List of Figures</i>	xiii
<i>List of Tables</i>	xxiii
Chapter 1: Introduction and Background	1-29
1.1. Introduction	1
1.2. Literature review	6
1.2.1. Microfluidic fuel cell	6
1.2.2. Oxygen reduction reaction	10
1.2.3. Carbon nitride and nanofibers	14
1.2.4. Electrospinning	17
1.3. Objectives of the thesis	19
1.4. Thesis organization	20
References	20
Chapter 2: Electrospun Carbon Nitride Supported on Poly(vinyl)	31-54
Alcohol as an Electrocatalyst for Oxygen Reduction Reaction	
2.1. Introduction	31
2.2. Experimental	31
2.2.1. Materials	31
2.2.2. Preparation of CN _x nanoparticles	32

2.2.3. Electrospinning	32
2.2.4. Physical Characterization	33
2.2.5. Working electrode preparation	33
2.2.6. Electrochemical characterization for oxygen reduction reaction	34
2.2.7. Scanning electrochemical microscopy	36
2.3. Results and discussions	36
2.3.1. SEM and TEM	36
2.3.2. FTIR	38
2.3.3. XPS	40
2.3.4. Raman spectroscopy	41
2.3.5. Voltammetry	42
2.3.6. <i>In-situ</i> FTIR voltammetry studies	47
2.3.7. Scanning electrochemical microscopy	52
2.4. Conclusion	53
References	54
Chapter 3: Electrocatalytic Activity of Electrospun Carbon Nitride- Polyacrylonitrile Nanofiber Towards Oxygen Reduction Reactions	55-70
3.1. Introduction	55
3.2. Experimental section	55
3.2.1. Synthesis of CN _x /PAN nanofibers	55
3.2.2. Physical and electrochemical characterization	56
3.3. Results and discussions	57
3.3.1. SEM and TEM	57
3.3.2. XPS	59
3.3.3. BET measurements	60

3.3.4. Scanning electrochemical microscopy	60
3.3.5. Linear sweep voltammetry	61
3.3.6. <i>In-situ</i> FTIR with cyclic voltammetry	63
3.3.7. Raman spectroscopy	64
3.3.8. RRDE studies	65
3.3.9. Durability studies (LSV)	67
3.4. Conclusions	69
References	69
Chapter 4: Improvement in Electrocatalytic Activity of Oxygen Reduction	
Reaction of Electrospun Carbon Nitride/Polyacrylonitrile Nanofibers by	71-95
Addition of Carbon Black and Nafion® Fillers	
4.1. Introduction	71
4.2. Experimental	71
4.2.1. Materials	71
4.2.2. Synthesis of CN _x nanofibers	72
4.2.3. Physical characterization	72
4.2.4. Electrochemical characterization for oxygen reduction reaction	73
4.2.5. Scanning electrochemical microscopy	73
4.3. Results and discussions	73
4.3.1. TEM and SEM	73
4.3.2. XPS	75
4.3.3. Voltammetry	76
4.3.4. RRDE studies	77
4.3.5. <i>In-situ</i> FTIR studies with cyclic voltammetry	79
4.3.6. Durability studies (LSV) with <i>in-situ</i> FTIR voltammetry	81

4.3.7. Raman studies	83
4.3.8. Scanning electrochemical microscopy	84
4.4. CN_x nanofibers as cathode catalyst for direct formic acid PEM fuel cell	87
4.4.1. Experimental section	87
4.4.1.1. CN _x nanofibers synthesis, characterization and half cell studies	87
4.4.1.2. Direct formic acid PEM fuel cell testing	88
4.4.2. Results and discussions	89
4.4.2.1. KMnO ₄ as oxidant in fuel cell testing	89
4.4.2.2. Direct formic acid PEM fuel cell results	91
4.4.3. Conclusions	93
References	93
Chapter 5: Direct Formic Acid Microfluidic Fuel Cell that Utilises Electrospun Carbon Nitride Nanofibers as Cathode Catalyst	95-113
5.1. Introduction	95
5.2. Experimental section	96
5.2.1. Fabrication of microfluidic fuel cell	96
5.2.2. Flow interfacial studies and MFC activity measurements	99
5.3. Results and discussions	101
5.3.1. CN _x nanofibers as cathode catalyst	101
5.3.2. Flow behaviour and MFC operation	105
5.4. Conclusions	112
References	113
Chapter 6: Conclusions and Future Prospects	115-118
6.1. Conclusions	115
6.2. Future prospects	117

References	118
Appendix A: Electrocatalytic Activity of Electrospun Carbon Nitride-Polyacrylonitrile Nano Fibre Towards Oxygen Reduction Reactions	119-121
Appendix B: Reduction mechanism of potassium permanganate on carbon nitride, platinum and gold catalyst	123-124
Curriculum Vitae	125-126

List of Figures

Figure No.	Title	Page No.
Figure 1.1	Schematic of hydrogen-oxygen fuel cell	2
Figure 1.2	Schematic of microfluidic fuel cell	3
Figure 1.3	The possible N-configurations in N-containing carbon materials; N1: pyridinic N, N2: pyrrolic N, N3, N4: graphitic N and N5: oxidized pyridinic N	13
Figure 1.4	The N-configurations: N1: pyridinic N, N2: pyrrolic N in the synthesized carbon nitride nanoparticles	14
Figure 1.5	Graphitic carbon nitride structure as suggested by Kroke et al.	15
Figure 1.6	Schematic of electrospinning process	18
Figure 1.7	Chemical structure of (a) PVA and (b) PAN	18
Figure 2.1	<i>In-situ</i> FTIR setup used to carry out <i>in-situ</i> FTIR with cyclic voltammetry	34
Figure 2.2	(a) SEM image of CN _x , (b) TEM image of CN _x , (c) SEM image of CN _x /PVA nanofibers (d) TEM image of CN _x /PVA nanofibers showing nanofibers of diameter ~ 150 nm, (e) TEM image of CN _x /PVA nanofibers with CN _x nanoparticles embedded in the CN _x /PVA nanofibers and (f) TEM image of CN _x /PVA nanofibers with CN _x nanoparticles entrapped within two aligned nanofibers	37
Figure 2.3	FTIR of native CN _x nanoparticles, PVA nanofibers and CN _x /PVA nanofibers	39

Figure 2.4	XPS spectra of CN _x nanoparticles for (a) C1s peaks and (b) N1s peaks; XPS spectra of CN _x /PVA nanofibers for (c) C1s and (d) N1s peaks	41
Figure 2.5	Raman spectra at 514.5 nm wavelength of native CN _x nanoparticles, CN _x /PVA nanofibers and PVA nanofibers, (b) Raman spectrum of CN _x nanoparticles: Raw data and smoothed data	42
Figure 2.6	(a) Linear sweep voltammograms of CN _x /PVA nanofibers (catalyst ink) CN _x /PVA-AP nanofibers, native CN _x nanoparticles, Pt/C, PVA nanofibers and bare glassy carbon electrode in 0.5 M H ₂ SO ₄ solution at scan rate of 20 mV s ⁻¹ for ORR. (b) Expanded portion (I) of the voltammograms of native CN _x nanoparticles, PVA nanofibers and bare glassy carbon electrode	44
Figure 2.7	Linear sweep voltammograms of CN _x /PVA nanofibers for ORR showing the variation of current density with rotation speed and that of Pt/C at 1600 RPM on a rotating ring disc glassy carbon electrode in 0.5 M H ₂ SO ₄ solution at scan rate of 20 mV s ⁻¹ : (a) Disk current; (b) Ring current; (c) number of electrons exchanged versus voltage for CN _x /PVA nanofibers (equation 2.1) and (d) Koutecky Levich plot for ORR for CN _x /PVA nanofibers (equation 2.2)	45
Figure 2.8	(a) <i>In-situ</i> FTIR spectra at potentials 0.9 V, 0.8 V, 0.7 V, 0.6 V and 0.5 V with (b) cyclic voltammetry of CN _x /PVA nanofibers in nitrogen and oxygen purged 0.5 M H ₂ SO ₄ for ORR. Expanded	48

portion of FTIR bands: (c) X at 3410 cm^{-1} (d) Y at 2590 cm^{-1} and (e) Z at 1980 cm^{-1}

Figure 2.9	Plot of band X at 3410 cm^{-1} vs potential (mV) of <i>in-situ</i> FTIR spectrum of CN_x/PVA nanofibers in O_2 saturated H_2SO_4 corresponding to CV shown in figure 2.7 (a)	49
Figure 2.10	(a) Polarization curves of CN_x/PVA nanofibers for ORR at different LSV repetitions and (b) FTIR spectra observed at 700 mV at different LSV repetitions	50
Figure 2.11	TEM images of CN_x/PVA nanofibers dispersed in isopropyl alcohol (a) before ORR voltammetry (b) 2000 LSV repetitions for ORR and (c) 5000 LSV repetitions for ORR	51
Figure 2.12	(a) Current-distance curve as the Pt microelectrode ($25\text{ }\mu\text{m}$) is approaching the CN_x/PVA nanofibers coated carbon paper and blank carbon paper, (b) SECM plot showing variation of current with electrode area surface (XY) keeping the height (Z) constant	52
Figure 3.1	TEM image of (a) native CN_x nanoparticles and (b) CN_x/PAN nanofibers	58
Figure 3.2	SEM image of (a) CN_x/PAN nanofibers and (b) PAN nanofibers	58
Figure 3.3	XPS spectra of N1s region for CN_x/PAN nanofibers. The dot lines represent the raw data for the XPS	59
Figure 3.4	N_2 sorption isotherm of CN_x/PAN nanofibers	60
Figure 3.5	(a) Current-distance curve as the Pt microelectrode ($25\text{ }\mu\text{m}$) is approaching the CN_x/PAN nanofibers coated carbon paper and blank carbon paper, (b) SECM plot showing variation of current with electrode area surface (XY) keeping the height (Z) constant	61

Figure 3.6	Linear sweep voltammograms of CN _x /PAN nanofibers, native CN _x nanoparticles, Pt/C and bare glassy carbon electrode in 0.5 M H ₂ SO ₄ solution at scan rate of 20 mV s ⁻¹ for ORR	62
Figure 3.7	(a) Cyclic voltammogram of CN _x /PAN nanofibers in nitrogen and oxygen purged 0.5 M H ₂ SO ₄ for ORR. FTIR bands of <i>in-situ</i> FTIR spectra at potentials 0.9 V, 0.8 V, 0.7 V, 0.6 V and 0.5 V: (b) X at 3420 cm ⁻¹	63
Figure 3.8	Raman spectra at 514.5 nm wavelength of CN _x /PAN nanofibers (before and after cyclic voltammetry), PAN nanofibers and native CN _x nanoparticles (inset)	65
Figure 3.9	Linear sweep voltammograms of CN _x /PAN nanofibers for ORR showing the variation of current density with rotation speed on a rotating ring disc glassy carbon electrode in 0.5 M H ₂ SO ₄ solution at scan rate of 20 mV s ⁻¹ : (a) Disk current; (b) Ring current; and (c) Koutecky Levich plot for ORR for CN _x /PAN nanofibers; and (d) number of electrons exchanged vs voltage	66
Figure 3.10	(a) Polarization curves of CN _x /PAN nanofibers for ORR at different LSV repetitions and (b) FTIR spectra observed at 700 mV at different LSV repetitions	68
Figure 4.1	SEM image of (a) CN _x nanofibers, (b) PAN/CB/Nafion [®] nanofibers	74
Figure 4.2	TEM image of CN _x nanofibers	74
Figure 4.3	XPS spectra of CN _x nanofibers: (a) wide scan with S 2p core level spectrum shown in inset, (b) N 1s core level spectrum	75

- Figure 4.4 Linear sweep voltammograms of CN_x nanofibers, CN_x/PAN nanofibers, native CN_x nanoparticles, Pt/C and bare glassy carbon electrode in 0.5 M H₂SO₄ solution at scan rate of 20 mV s⁻¹ for ORR 77
- Figure 4.5 Linear sweep voltammograms of CN_x nanofibers for ORR showing the variation of current density with rotation speed on a rotating ring disc glassy carbon electrode in 0.5 M H₂SO₄ solution at scan rate of 20 mV s⁻¹: (a) Disk current; (b) Ring current; and (c) Koutecky Levich plot for ORR for CN_x nanofibers 79
- Figure 4.6 (a) Cyclic voltammogram of CN_x nanofibers in nitrogen and oxygen purged through 0.5 M H₂SO₄ for ORR. FTIR bands of *in-situ* FTIR spectra at potentials 1.2 V, 1 V, 0.9 V, 0.8 V and 0.7 V: (b) X at 3490 cm⁻¹ (c) Y at 1950 cm⁻¹ and (d) Z at 2620 cm⁻¹ 80
- Figure 4.7 (a) Polarization curves of CN_x nanofibers for ORR at different LSV repetitions and (b) FTIR spectra observed at 700 mV at different LSV repetitions 82
- Figure 4.8 Raman spectra at 514.5 nm wavelength of CN_x nanofibers (before and after CV), PAN/CB/Nafion[®] nanofibers and native CN_x nanoparticles (inset) 84
- Figure 4.9 (a) Current-distance curve as the Pt microelectrode (25 μm) is approaching the CN_x nanofibers coated carbon paper, CN_x/PAN nanofibers coated carbon paper and blank carbon paper, (b) 86

	SECM plot showing variation of current with electrode area surface (XY) keeping the height (Z) constant	
Figure 4.10	PEM fuel cell setup	88
Figure 4.11	Polarisation curve comparison for different oxidants, e.g., O ₂ and 0.144 M KMnO ₄ + 0.5 M H ₂ SO ₄ (1:20); Anode: Pt black; Cathode: CN _x nanofibers (0.5 mg cm ⁻²); Fuel: 2.1 M HCOOH	90
Figure 4.12	Linear sweep voltammograms for KMnO ₄ reduction: (a) CN _x nanofibers, Pt black and bare glassy carbon electrode in 0.5 M H ₂ SO ₄ + 0.144 M KMnO ₄ solution, (b) CN _x nanofibers in 0.5 M H ₂ SO ₄ + 0.144 M KMnO ₄ and 0.5 M H ₂ SO ₄ + 0.144 M KMnO ₄ + 2.1 M HCOOH solutions to study HCOOH poisoning	90
Figure 4.13	Current density-voltage and power density curves at different 0.5 M H ₂ SO ₄ + 0.144 mM KMnO ₄ (oxidant) flow rates with formic acid (fuel) at 3 mL/min for (a) CN _x nanofibers (0.5 mg cm ⁻²), (b) Carbon paper as cathode catalyst. Anode used is Pt black	91
Figure 4.14	Current density-voltage and power density curves for Pt black (0.5 mg cm ⁻²), CN _x nanofibers (0.5 mg cm ⁻²) and carbon paper as cathode catalysts with formic acid (fuel) flow rate of 3 mL/min and 0.5 M H ₂ SO ₄ + 0.144 mM KMnO ₄ (oxidant) flow rate of 30 mL/min. Anode: Pt black	92
Figure 5.1	Y-shaped microfluidic fuel cell with microchannel of dimensions 800 μm (W) x 125 μm (H) x 3.7 cm (L); anode (width 300 μm) and cathode (width 300 μm). Distance between the electrodes 100 μm such that interfacial layer lies within this region	97

Figure 5.2	Fabrication steps of microfluidic fuel cell: (a) UV-lithography of OFPR and LOR resist to define anode coating, (b) Electron beam deposition of 10 nm Ti and 50 nm Pt film followed by lift-off using PG remover, (c) UV-lithography to define cathode coating aligned with the anode, (d) Electron beam deposition of 10 nm Ti and 50 nm Au film followed by coating of CN _x nanofibers by electrospinning and lift-off using PG remover, (e) UV-lithography of SU-8 resist on Si wafer, (f) PDMS casting, (g) PDMS demoulding and (h) Alignment of PDMS microchannel on top of the electrodes coated glass slide	99
Figure 5.3	(a) Assembled microfluidic fuel cell; Microscopic images (b) Y-junction of the microchannel (region I in Figure 5.3 (a)) and (c) the middle part of the microchannel (region II in Figure 5.3 (a)). Left electrode is gold cathode and right electrode is platinum anode patterned on glass surface	102
Figure 5.4	(a) Schematic of microfluidic fuel cell during cell testing; (b) Actual photograph of microfluidic fuel cell experimental set-up	103
Figure 5.5	(a) SEM and (b) TEM of CN _x nanofibers	104
Figure 5.6	Optical microscopic (a) bright field image and (b) dark field image of CN _x nanofibers as cathode catalyst on Au surface after lift-off. Bright field image of (c) bare Au and (d) Pt as cathode. Dark field image of CN _x nanofibers as cathode catalyst (e) before lift-off and (f) after lift-off	105
Figure 5.7	SEM of a single cluster of CN _x catalyst after lift-off	106

Figure 5.8	XPS spectra of CN _x nanofibers: wide scan spectra (a) before lift-off, (b) after lift-off, N 1s core level spectra (c) before lift-off and (d) after lift-off	107
Figure 5.9	(a) Width of the interface of the fuel and oxidant flow in the microchannel at different flow rates of the fluids at the middle (X = 18 mm) and near the outlet (X = 36 mm) of the microchannel. The black horizontal line indicates the distance between the electrodes; (b) Snapshot and (c) Plot profile of the microchannel near the outlet when fluid is flowing at the flow rate of 300 $\mu\text{L min}^{-1}$	109
Figure 5.10	Microfluidic fuel cell polarization curve and power density curve at different flow rates of 300, 400 and 500 $\mu\text{L min}^{-1}$ with the cathode catalyst: (a) CN _x nanofibers, (b) Pt and (c) Au	112
Figure 5.11	Microfluidic fuel cell polarization curve and power density curve at flow rate of 300 $\mu\text{L min}^{-1}$ for different cathode catalysts: CN _x nanofibers, Pt and Au	113
Figure A1	XPS spectra of N1s region for (a) native CN _x nanoparticles and (b) PAN nanofibers. The dot lines represent the raw data for the XPS	121
Figure A2	Linear sweep voltammograms of CN _x /PAN nanofibers at CN _x loading of 500, 402, 304 and 102 $\mu\text{g cm}^{-2}$ in 0.5 M H ₂ SO ₄ solution at scan rate of 20 mV s ⁻¹ for ORR	122
Figure A3	FTIR bands of <i>in-situ</i> FTIR spectra with cyclic voltammogram of CN _x /PAN nanofibers in oxygen purged 0.5 M H ₂ SO ₄ for ORR	122

at potentials 0.9 V, 0.8 V, 0.7 V, 0.6 V and 0.5 V: (a) Y at 1990 cm^{-1} and (b) Z at 2710 cm^{-1}

Figure B1 Cyclic voltammograms for KMnO_4 reduction on CN_x nanofibers, Pt and Au in 0.5 M H_2SO_4 + 0.144 M KMnO_4 solution 126

List of Tables

Table No.	Title	Page No.
Table 1.1.	Literature on formic acid microfluidic fuel cell that uses dissolved oxygen streams and potassium permanganate as oxidant. The comparison for MFC performance for platinum and non-platinum cathode catalysts is presented	7
Table 1.2.	Thermodynamic electrode potentials of electrochemical O ₂ reductions	11
Table 2.1.	Comparison of onset potential and peak current density of CN _x /PVA nanofibers, native CN _x nanoparticles and Pt/C	45
Table 3.1.	Onset potentials and peak current densities of CN _x /PAN nanofibers, native CN _x nanoparticles and Pt/C	62
Table 4.1.	Onset potentials and peak current densities of CN _x nanofibers, CN _x /PAN nanofibers, native CN _x nanoparticles and Pt/C	77
Table 5.1.	Performance characteristics of microfluidic fuel cell for different cathode catalysts (1 mg cm ⁻² , 50 nm); Anode: Pt (50 nm), Anolyte: 2.1 M HCOOH; Catholyte: 0.144 M KMnO ₄ ; Supporting electrolyte: 0.5 M H ₂ SO ₄	114