

## CONTENTS

<i>Abstract</i>	i - vi
<i>Declaration</i>	vii
<i>Certificates</i>	viii-ix
<i>Dedication</i>	x
<i>Acknowledgements</i>	xi - xii
<i>Contents</i>	xiii - xviii
<i>List of tables</i>	xix
<i>List of figures</i>	xx - xxx
<i>List of abbreviations</i>	xxxii - xxxiii
<i>List of symbols</i>	xxxiii- xxxiv
<b>CHAPTER I</b>	[1-38]
<b>Introduction</b>	
1.1 Overview of fuel cell	1
1.2 Direct methanol fuel cell (DMFC)	2-23
1.2.1 Operating principle of DMFC	2-3
1.2.2 Methanol oxidation reaction (MOR) mechanism	4
1.2.3 Applications of DMFC	4-5
1.2.3.1 Transport applications	5
1.2.3.2 Portable applications	5
1.2.4 Components of DMFC	5-9
1.2.4.1 Electrode	6-7
1.2.4.2 Gas diffusion layer	7-8
1.2.4.3 Catalyst layer	8-9
1.2.4.4 Electrolyte membrane	9
1.2.5 Challenges related to DMFC	10-11
1.2.5.1 Methanol crossover	10
1.2.5.2 Sluggish electrooxidation kinetics	10-11
1.2.5.3 Use of platinum as electrocatalyst	11
1.2.6 Non-noble metal based anode materials for DMFC	11-23
1.2.6.1 Transition metal oxide	11-12
1.2.6.2 Carbon material	13-18
1.2.6.2.1 Carbon quantum dot	13
1.2.6.2.2 Carbon black	14

1.2.6.2.3 Mesoporous carbon	14-15
1.2.6.2.4 Carbon nanofibres	15
1.2.6.2.5 Carbon nanotubes	16
1.2.6.2.6 Graphene	16-18
1.2.6.3 Conducting polymers	18-21
1.2.6.3.1 PEDOT:PSS as promising conducting polymer	20-21
1.2.6.4 Nanocomposite anode catalysts for methanol oxidation	21-23
1.2.6.4.1 Binary nanocomposites	21-22
1.2.6.4.2 Ternary nanocomposites	22-23
1.3 Scope of the thesis and statement of thesis problem	23-25
1.4 References	26-38
<b>CHAPTER II</b>	[39-74]
<b>Theoretical aspects</b>	
2.1 Basic concepts of electrochemistry	39-44
2.1.1 Electrochemical cell	39-41
2.1.2 Faradaic and non-faradaic Processes	41-42
2.1.3 The electrode and electrolyte interface	42-43
2.1.4 Electrode reaction mechanism	43-44
2.2 Cyclic voltammetry	44-51
2.2.1 Surface coverage of adsorbed redox active species	47-48
2.2.2 Laviron's Theory	48-51
2.2.2.1 Calculation of heterogeneous rate constant ( $k_s$ ) and electron transfer coefficient ( $\alpha$ )	51
2.3 Butler-Volmer kinetics	51-56
2.3.1 Tafel analysis	55-56
2.4 Electrochemical Impedance Spectroscopy (EIS)	56-62
2.4.1 Different impedance parameters in an electrochemical cell system	60-62
2.5 Chronoamperometry (CA)	62-64
2.6 The Brunauer-Emmett-Teller (BET) Theory	64-67
2.7 The Barrett, Joyner and Halenda (BJH) method	67-69
2.8 References	70-74

<b>CHAPTER III</b>	[75-106]
<b>Experimental techniques</b>	
3.1 Materials	75-77
3.2 Synthesis of reduced graphene oxide (rGO), PEDOT:PSS and manganese dioxide (MnO <sub>2</sub> ) nanorod based ternary nanocomposite	77-82
3.2.1 Synthesis of graphite oxide (GO)	77-78
3.2.2 Synthesis of $\alpha$ -MnO <sub>2</sub> nanorods	78-79
3.2.2.1 Formation mechanism of $\alpha$ -MnO <sub>2</sub> nanorods	79
3.2.3 Synthesis of PEDOT:PSS/MnO <sub>2</sub> nanocomposite	79-80
3.2.4 Synthesis of rGO/PEDOT:PSS/MnO <sub>2</sub> nanocomposite	80-81
3.2.4.1 Formation mechanism of rGO/PEDOT:PSS/MnO <sub>2</sub> nanocomposite	81-82
3.3 Synthesis of reduced graphene oxide (rGO), PEDOT:PSS and nickel oxide (NiO) based ternary nanocomposite	82-86
3.3.1 Synthesis of NiO nanoplate-nanorod structure	82-83
3.3.1.1 Formation mechanism of NiO nanoplate-nanorod structure	83-84
3.3.2 Synthesis of PEDOT:PSS/NiO nanocomposite	84
3.3.3 Synthesis of rGO/PEDOT:PSS/NiO nanocomposite	85-86
3.3.3.1 Formation mechanism of rGO/PEDOT:PSS/NiO nanocomposites	86
3.4 Synthesis of reduced graphene oxide (rGO), PEDOT:PSS and nickel manganese spinel oxide (NiMn <sub>2</sub> O <sub>4</sub> ) based ternary nanocomposite	87-91
3.4.1 Synthesis of NiMn <sub>2</sub> O <sub>4</sub> nanoparticles	87-88
3.4.1.1 Formation mechanism of NiMn <sub>2</sub> O <sub>4</sub> nanoparticles	88
3.4.2 Synthesis of PEDOT:PSS/NiMn <sub>2</sub> O <sub>4</sub> nanocomposite	88-89
3.4.3 Synthesis of rGO/PEDOT:PSS/ NiMn <sub>2</sub> O <sub>4</sub> nanocomposite	89-90
3.4.3.1 Formation mechanism of rGO/PEDOT:PSS/ NiMn <sub>2</sub> O <sub>4</sub> nanocomposite	90-91
3.5 Preparation of nanohybrid electrodes	91
3.6 Characterization techniques	91-101
3.6.1 Scanning electron microscopy	91-93
3.6.2 High resolution transmission electron microscopy	93-95
3.6.3 X-ray diffraction	95-97
3.6.4 Raman spectroscopy	97-98
3.6.5 X-ray photoelectron spectroscopy	98-100
3.6.6 N <sub>2</sub> adsorption-desorption measurements	100-101

3.7 Measurements of electrochemical properties	101-103
3.7.1 Cyclic voltammetry	102
3.7.2 Linear sweep voltammetry	102
3.7.3 Electrochemical impedance spectroscopy	103
3.7.4 Chronoamperometry	103
3.7.5 Cyclic stability study	103
3.8 References	104-106

## CHAPTER IV

<b>Reduced graphene oxide (rGO)/PEDOT:PSS/Manganese dioxide (MnO<sub>2</sub>) ternary nanocomposite as anode catalyst for methanol oxidation</b>	[107-139]
4.1 Introduction	107-109
4.2 Morphological characterizations	109-111
4.2.1 Scanning electron microscopy	109-110
4.2.2 Transmission electron microscopy	110-111
4.3 Physical Characterizations	111-118
4.3.1 X-ray diffraction	111-112
4.3.2 Raman spectroscopy	113-114
4.3.3 X-ray photoelectron spectroscopy	114-115
4.3.4 Nitrogen (N <sub>2</sub> ) adsorption-desorption analysis	116-118
4.4 Electrochemical characterizations	118-131
4.4.1 Electrochemical activity of the modified electrodes	118-123
4.4.1.1 Variation of anodic peak current (I <sub>pa</sub> ) and cathodic peak current (I <sub>pc</sub> ) vs. scan rate (v)	119-122
4.4.1.2 Variation of anodic peak potential (E <sub>pa</sub> ) and cathodic peak potential (E <sub>pc</sub> ) vs. scan rate (v)	122-123
4.4.2 Electrochemical activity of the electrodes towards methanol oxidation	123-126
4.4.3 Tafel analysis	126-127
4.4.4 Chronoamperometry and Cyclic stability test	127-128
4.4.5 Electrochemical impedance spectroscopy measurements after cyclic Stability test	128-129
4.4.6 Characterizations after Cyclic stability test	129-131
4.5 Summary	131-132
4.6 References	133-139

**CHAPTER V** [140-171]

**Reduced graphene oxide (rGO)/PEDOT:PSS/Nickel oxide (NiO) ternary nanocomposite as anode catalyst for methanol oxidation**

5.1 Introduction	140-141
5.2 Morphological characterizations	142-144
5.2.1 Scanning electron microscopy	142-143
5.2.2 Transmission electron microscopy	143-144
5.3 Physical Characterizations	144-150
5.3.1 X-ray diffraction	144-145
5.3.2 Raman spectroscopy	145-146
5.3.3 X-ray photoelectron spectroscopy	146-148
5.3.4 Nitrogen (N <sub>2</sub> ) adsorption-desorption analysis	148-150
5.4 Electrochemical characterizations	150-164
5.4.1 Electrochemical activity of the modified electrodes	150-155
5.4.1.1 Variation of anodic peak current (I <sub>pa</sub> ) and cathodic peak current (I <sub>pc</sub> ) vs. scan rate (v)	151-154
5.4.1.2 Variation of anodic peak potential (E <sub>pa</sub> ) and cathodic peak potential (E <sub>pc</sub> ) vs. scan rate (v)	154-155
5.4.2 Electrochemical activity of the electrodes towards methanol oxidation	155-158
5.4.3 Linear sweep voltammetry and Tafel analysis	159-160
5.4.4 Chronoamperometry and Cyclic stability test	160-161
5.4.5 Electrochemical impedance spectroscopy measurements after cyclic stability test	161
5.4.6 Characterizations after cyclic stability test	161-164
5.5 Summary	164-165
5.6 References	166-171

**CHAPTER VI** [172-204]

**Reduced graphene oxide (rGO)/PEDOT:PSS/Nickel Manganite (NiMn<sub>2</sub>O<sub>4</sub>) ternary nanocomposite as anode catalyst for methanol oxidation**

6.1 Introduction	172-174
6.2 Morphological characterizations	174-177
6.2.1 Scanning electron microscopy	174-176
6.2.2 Transmission electron microscopy	176-177
6.3 Physical Characterizations	177-183
6.3.1 X-ray diffraction	177-178

6.3.2 Raman spectroscopy	178-179
6.3.3 X-ray photoelectron spectroscopy	179-181
6.3.4 Nitrogen (N <sub>2</sub> ) adsorption-desorption analysis	181-183
6.4 Electrochemical characterizations	183-198
6.4.1 Electrochemical activity of the modified electrodes	183-188
6.4.1.1 Variation of anodic peak current (I <sub>pa</sub> ) and cathodic peak current (I <sub>pc</sub> ) vs. scan rate (v)	184-187
6.4.1.2 Variation of anodic peak potential (E <sub>pa</sub> ) and cathodic peak potential (E <sub>pc</sub> ) vs. scan rate (v)	187-188
6.4.2 Electrochemical activity of the electrodes toward methanol oxidation	188-192
6.4.3 Linear sweep voltammetry and Tafel analysis	192-193
6.4.4 Chronoamperometry and Cyclic stability test	193-195
6.4.5 Electrochemical impedance spectroscopy measurements after cyclic stability test	195
6.4.6 Characterizations after cyclic stability test	195-198
6.5 Summary	198-199
6.6 References	200-204
<b>CHAPTER VII</b>	[205-209]
<b>Conclusions and Future Prospects</b>	
7.1 Conclusion	205-209
7.2 Future prospects	209
<b>List of publications</b>	[210-211]