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Electrocatalytic and Charge Storage/Delivery Properties of Thin Ir/Ru-oxide Coatings

A thesis submitted to McGill University in partial fulfillment of the requirements of the degree

of

Doctor of Philosophy

By

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Abstract

Metal-oxide (MO) coatings have been used in many electrochemistry-based applications, such as in the chloro-alkali industry, particularly, for the production of various valuable chemicals (e.g chlorine, sodium hydroxide, oxygen, etc.). MO coatings have also been employed for other purposes, such as electrodes for electrochemical supercapacitors (SCs), corrosion protection of metals, neural-stimulating electrodes, sensor electrodes, and electrodes in organic synthesis and wastewater treatment.

This PhD thesis represents an attempt to contribute to the area of mixed metal-oxide (MMOs) electrodes by employing Ir/Ru-oxide coatings as electrode materials in four selected applications. The general objectives of this research were to develop bimetallic Ir/Ru-oxide coatings of various compositions on a titanium metal substrate through thermal decomposition and to investigate their properties in the area of charge delivery and storage and in hydrogenation electrocatalytic reactions.

Electrochemical and topographical/structural/morphological properties of thermally prepared Ir_x -Ru_{1-x}-oxide coatings of various compositions (x = 0, 0.2, 0.4, 0.6, 0.8, 1.0) formed on a Ti substrate were first investigated for its potential use as neural stimulating electrodes. All coating surfaces displayed a 'cracked-mud' morphology, yielding a high surface roughness. Among several compositions examined, the $Ir_{0.8}Ru_{0.2}$ -oxide coating was found to offer the largest apparent electrochemical active surface area (AEASA, 1540 cm⁻² per 1cm² of geometric area) and charge storage capacity (CSC, 27 mC cm⁻²). This CSC value is by ca. 56% higher than the current state-of-the-art neural stimulating electrode, Ir-oxide, making it a good candidate for further optimization and possible application as a neural stimulating electrode.

In addition to neural stimulating electrodes, the Ir/Ru-oxide coating was employed in the field of charge storage in supercapacitors (SCs). Pure ruthenium oxide (RuO₂) coating, the most common electrode material for SCs, showed relatively low performance as compared to bimetallic Ir_xRu_{1-x} -oxide coatings operated under the same experimental conditions applied. An electrochemically-activated $Ir_{0.4}Ru_{0.6}$ -oxide coating yielded the highest areal capacitance value (85 mF cm⁻²) at a galvanostatic charging/discharging current density of 0.1 mA cm⁻² (0.9 V potential window). A prolonged electrochemical cycling of the Ir/Ru-oxide coatings in corrosive phosphate buffered saline pH 7.4, performed within an extreme potential window of 5 V,

revealed an excellent stability of the coatings. In addition, this cycling procedure enabled a significant increase in capacitance for all coating compositions. It was shown that the areal capacitance of these coatings is strongly dependent upon the nature of the components of which the metal oxide is composed.

Since both Ru and Ir are known to be relatively good hydrogenation catalysts, an attempt was made to investigate the electrohydrogenation/electrocatalytic properties of the $Ir_{0.8}Ru_{0.2}$ -oxide coating in electrochemical hydrogenation reactions, namely in the reaction of (i) CO_2 reduction to usable organic chemicals, and in the reaction of (ii) regeneration of a very expensive enzyme co-factor, nicotinamide adenine dinucleotide, 1,4-NADH.

The electrochemical reduction of CO_2 on the $Ir_{0.8}Ru_{0.2}$ -oxide electrode was performed in in a batch electrochemical cell in an aqueous electrolyte (Briton Robinson buffer, pH=5.82) at various electrode potentials. The results showed that the Ir/Ru-oxide electrode can efficiently be used for the electrochemical conversion of CO_2 into different valuable organic molecules at high faradaic efficiency, 85% and 96% at 295 K and 277 K, respectively. Ethanol was found to be the major electrochemical reduction product remained in the liquid phase, with minor quantities of methanol, acetone and acetaldehyde. The amount of formed products and the corresponding faradaic efficiency were found to be strongly dependent on electrode potential. A maximum in both was obtained at -1.70 V vs. MSE. At this potential, lowering the reaction temperature from 295 K to 277 K was found to increase the CO_2 reduction kinetics only at short electrolysis times, while the corresponding faradaic efficiency increased significantly.

The final study on the applicability of the $Ir_{0.8}Ru_{0.2}$ -oxide coating as a cathode material concerned the direct electrochemical regeneration of enzymatically-active 1,4-NADH from its oxidized form NAD⁺. The results showed that the percentage of enzymatically-active 1,4-NADH present in the product mixture (i.e. the 1,4-NADH recovery) is highly dependent on the electrode potential, reaching a maximum (88 mol.%) at -1.70 V vs. MSE, which coincides with the faradaic maximum in the CO₂ reduction reaction, indicating that at this electrode potential a balance between the rate of formation of active hydrogen, H_{ads}, and its use in the subsequent hydrogen, H₂, is inhibited.

Résumé

Les revêtements de l'oxyde métallique ont été utilisés dans plusieurs applications d'électrochimie de base, particulièrement dans l'industrie du chlore-alcalins, pour la production de produits chimiques valables (le chlore, l'hydroxyde de sodium, l'oxygène, etc.). Ces couches d'oxyde métallique ont aussi été employées à des fins d'électrodes de supercondensateurs électrochimiques et en système organique de protection contre la corrosion des métaux, d'électrodes de stimulation neuronale, de capteurs d'électrodes et traitement de gaspillage d'eau.

Cette thèse de doctorat représente une tentative afin de contribuer à la zone d'électrodes de l'oxyde métallique en utilisant les couches de l'Ir/Ru-oxyde comme matériels d'électrode en quatre applications sélectionnées. Les objectifs généraux de cette recherche étaient de développer les couches Ir/Ru-oxyde bimétallique des compositions variables sur un substrat de métal de titane à travers une décomposition thermique et de surveiller leurs propriétés dans la zone de délivrance de charge et de stockage ainsi que dans des recherches d'hydrogénation électro-catalytique.

Les propriétés électrochimique, topographique, structurel et morphologique des compositions variables de couches d'Ir/Ru-oxyde (x = 0, 0.2, 0.4, 0.6, 0.8, 1.0) thermiquement préparées formées sur un substrat d'Ir/Ru-oxyde ont tout d'abord été enquêtées sur leur utilisation potentielle comme étant des électrodes de stimulation neurale. Toutes les couches de surface ont affichés sur une morphologie 'boue-craquelée', ce qui donne une haute surface de rugosité. Entre certaines compositions examinées, la couche du Ir/Ru-oxyde a été celle ayant offert la plus grande zone de surface électrochimique active (AEASA, 1540 cm⁻² par 1 cm⁻² de zone géométrique) et de capacité de stockage de charge (CSC, 27 mC cm⁻²). Cette valeur de CSC est 56 % plus élevée que l'électrode neurale de l'état de l'art de stimulation courante, Ir-oxyde, ce qui en fait un bon candidat pour une future optimisation et possibilité d'application comme étant un électrode de stimulation neurale.

En plus des électrodes de stimulation neurale, la couche de l' Ir/Ru-oxyde a été employée dans le domaine du stockage de charge dans les supercondensateurs. La couche de l'oxyde de ruthénium pur, étant le matériel d'électrode le plus commun du supercondensateurs, a relativement montré une basse performance comparé au revêtement du Ir/Ru-oxyde bimétallique

exploité sous les mêmes conditions expérimentales appliquées. Une couche de $Ir_{0.4}Ru_{0.6}$ -oxyde électrochimiquement activée a donné la valeur la plus élevée de la capacité surfacique (85 mF cm⁻²) dans une densité de courant galvanostratique chargée/déchargée de 0.1 mA cm⁻² (0.9 V de fenêtre potentielle). Un cycle électrochimique prolongé des couches de l' Ir/Ru-oxyde au-delà d'une solution saline tamponnée au phosphate corrosif pH 7.4, ayant performé une fenêtre de potentiel extrême de 5 V, a révélé une excellente stabilité des revêtements. De plus, cette procédure de cyclisme a permis une augmentation significative de la capacité pour toutes les compositions de revêtements. Il a été démontré que la capacitance surfacique de la nature des composantes par laquelle l'oxyde métallique est composé.

Puisque le Ru et le Ir, tous les deux, sont reconnus à être relativement de bons catalyseurs d'hydrogénation, une tentative a été mise en place afin d'enquêter les propriétés de la couche du $Ir_{0.4}Ru_{0.6}$ -oxyde au-delà des réactions d'hydrogénation électrochimique, à savoir dans la réaction de la réduction du CO₂ à des produits chimiques organiques utilisables ainsi que dans la réaction de régénération d'un co-facteur enzymatique très cher, le nicotinamide adénine dinucleotide (1.4-NADH).

La réduction électrochimique du CO_2 sur l'électrode de l'Ir_{0.4}Ru_{0.6}-oxyde a été interprété dans une cellule électrochimique en discontinu dans un électrolyte aqueux (le tampon Robinson Britannique, pH=5.82) à divers potentiels d'électrode. Les résultats obtenus montrent que l'électrode Ir/Ru-oxyde peut efficacement être utilisé dans la conversion électrochimique du CO_2 dans différentes molécules organiques de valeur à haut rendement faradique, respectivement entre 85% et 96% à 295 K et 277 K. On remarque que l'éthanol est le produit de réduction électrochimique majeure demeuré de la phase liquide, avec des quantités minimes de méthanol, d'acétone et d'acétaldéhyde. On remarque que la quantité de produits formés et le rendement faradique correspondant dépendent fortement sur l'électrode potentiel. Le maximum obtenu dans les deux est de -1.70 V vs MSE. À ce niveau, on remarque que l'abaissement de la température de réaction de 295 K à 277 K augmente la cinétique de réduction du CO₂ seulement à des temps d'électrolyse courts, tandis que le rendement faradique correspondant augmente significativement. La dernière étude de l'application de la couche de l' $Ir_{0.4}Ru_{0.6}$ -oxyde comme matériel de cathode concerne la régénération électrochimique directe du 1.4-NADH enzymatiquement actif de sa forme oxydée, NAD⁺. Les résultats ont démontré que le pourcentage du 1.4-NADH enzymatiquement actif présent dans le mélange du produit (la récupération du 1.4-NADH) est fortement dépendante du potentiel d'électrode, atteignant un maximum (88 mol. %) à -1,70 V vs MSE, ce qui coïncide avec la faradique maximale dans la réaction de réduction des émissions de CO_2 , indiquant à ce potentiel d'électrode, qu'un équilibre entre la vitesse de formation de l'hydrogène actif, H_{ads} , et son utilisation dans la réaction d'hydrogénation ultérieure de la molécule organique, est atteinte, tandis que son hydrogène gazeux de réduction, H_2 , est inhibée.

Acknowledgements

A large amount of gratitude is owed to my late mother, who died during the period when I was in the middle of this journey. She never stopped praying for me and kept supporting me until the very end.

I would also like to express my sincere gratitude and deepest appreciation to my supervisor, Prof. Sasha Omanovic, for his excellent guidance, support, patience, and availability which played an essential role in providing excellent atmosphere for me in my research tasks. This work would have never been possible without his utmost assistance and contribution.

I am thankful to all members of the Electrochemistry/Corrosion Research Group at the Department of Chemical Engineering, McGill (Mario, Mark, Mehdi, Sajjad, Saloumeh, Jacob, Emmanuel and especially Mahmoud Rammal) for their help and support during the research. I am also grateful to all of my friends Salman, Sagheer, Laiq and Mohan. I would like to express my sincere gratitude and whole-heartedly feelings to Irshad Ali, Mahmoud Rammal, Maggie Taher and Saad Ghareba for giving support in times of need. I also emphasize the contribution of my summer research students (Joan, Saikat and Maëlle) to my research work and appreciate their support during the period. I want also to use this opportunity to thank departmental technical staff Frank, Ranjan, Andrew, Gerald, Lu, Emily, Louise and Jo-Ann for all the relentless help they provided during my research.

Lastly, I can not forget my great life partner, my wife Ana, who has been a very supportive, caring and patient companion for me during the past few years in research. The presence of my loving family and lovely daughters, Guloona, Zarghoona and son Raza, facilitated my work and pushed me always to achieve excellence.

Table	of	Contents
-------	----	----------

Abstract	i
Résumé	iii
Acknowledgements	vi
Nomenclature	xvii
CHAPTER 1	1
1. Introduction	1
CHAPTER 2	
2. Background and Literature Review	4
2.1 Iridium-Ruthenium Oxide Coatings as Neural Stimulating Electrodes	4
2.1.1 Neural prosthetics	4
2.1.2 Neural electrodes	5
2.1.2.1 Neural stimulating electrodes	6
2.1.2.2 Requirements of materials used for neural stimulating electrodes and challenges	8
2.1.2.3 Neural stimulating electrodes materials and charge injection mechanisms	9
2.1.2.4 Capacitive/non-faradaic charge injection materials	
2.1.2.5 Capacitive/faradaic charge injection materials	11
2.1.2.6 New emerging materials	
2.1.2.7 Hybrid electrode materials	
2.2 Iridium-Ruthenium-oxide Coatings for Supercapacitors	14
2.2.1 Capacitors	14
2.2.2 Supercapacitors (SCs)	15
2.2.2.1 Types of Supercapacitors	16
2.2.2.2 Material used for supercapacitors (SCs)	
2.3 Iridium-Ruthenium-oxide Coatings for the Electrochemical Reduction of CO ₂	20
2.3.1 Overview	
2.3.2 Electrode material for CO ₂ reduction	
2.3.3 Governing factors of the CO ₂ reduction reaction	
2.3.3.1 Effects of supporting electrolytes	23
2.3.3.2 The effect of pH	
2.3.3.3 Temperature	
2.3.3.4 Pressure	
2.4 Electrochemical Reduction of NAD ⁺ to enzymatically-active 1,4-NADH	

2.4.1	Coenzyme nicotinamide adenine dinucleotide, NAD(H)	29
2.4.2	Regeneration of 1,4-NADH	
2.5 Mi	xed Metal-Oxide Coatings (MMO)	
2.5.1	Development of mixed metal-oxide coatings (MMO) through thermal decomposition	
2.5.1	1.2 Metal-oxide coating electrodes	
СНАРТ	ГЕ R 3	
3. State	ment of Objectives	
СНАРТ	ΓER 4	
Large	Charge-Storage-Capacity Iridium/Ruthenium Oxide Coatings as	Promising
Materia	al for Neural Stimulating Electrodes	
4.1 Pre	eface	
4.2 Ab	ostract	
4.3 Int	roduction	
4.4 Ex	perimental	
4.4.1	Chemicals and reagents	
4.4.2	Electrode preparation	
4.4.3	Electrochemical measurements	41
4.4.4	Surface characterization	
4.5 Re	sults and discussions	
4.5.1	Surface morphology/topography and XRD analysis	
4.5.2	Electrochemical measurements	
4.5.3	Charge storage capacity (CSC)	
4.6	Conclusions	
4.7	Acknowledgments	
СНАРТ	Γ ΕR 5	
Iridium	-Ruthenium-oxide Coatings for Supercapacitors	
5.1 Pre	eface	
5.2 Ab	ostract	59
5.3 Int	roduction	
5.4 Ex	perimental	
5.4.1	Chemicals and reagents	
5.4.2	Electrode preparation	

5.4.3 Electrochemical capacitance measurements	63
5.5 Results and discussions	64
5.5.1 Surface topography/morphology	64
5.5.2 Coating stability and activation	66
5.5.3 Capacitive behavior of the coatings	67
5.5.4 Electrochemical impedance spectroscopy (EIS)	76
5.6 Conclusions	. 77
5.7 Acknowledgements	78
CHAPTER 6	79
Electrochemical Reduction of CO ₂ in an Aqueous Electrolyte Employing	an
Iridium/Ruthenium-oxide Electrode	79
6.1 Preface	79
6.2 Abstract	80
6.3 Introduction	81
6.4 Experimental	84
6.4.1 Chemicals and reagents	84
6.4.2 Electrode preparation	84
6.4.3 Electrochemical reduction of CO ₂	85
6.5 Results and discussion	86
6.5.1 Surface topography	86
6.5.2 Linear polarization measurements	87
6.5.3 Electrolysis measurements	88
6.5.4 Effect of temperature on the electrochemical reduction of CO ₂	90
6.5.5 Effect of electrode potential on the electrochemical reduction of CO ₂	92
6.5.6 Electrode surface fouling	95
6.6 Conclusions	. 98
6.7 Acknowledgements	. 98
CHAPTER 7	. 99
Direct Electrocatalytic Reduction of Coenzyme NAD ⁺ to Enzymatically-active 1,4-NA	DH
Employing an Iridium/Ruthenium-oxide Electrode	. 99
7.1 Preface	. 99
7.2 Abstract	100

7.3 Introduction	01
7.4 Materials and methods	03
7.4.1 Ir/Ru-oxide coating/electrode preparation1	03
7.4.2 Electrochemical regeneration of 1,4-NADH1	04
7.5 Result and discussion	05
7.5.1 Surface morphology of the Ir _{0.8} Ru _{0.2} -oxide coating1	05
7.5.2 Reduction of NAD ⁺ on a Ir/Ru-oxide electrode (1,4-NADH regeneration)	06
7.6 Conclusions	10
7.7 Acknowledgements	11
CHAPTER 8	12
8. Conclusions1	12
8.1 Electrochemical and topographical/structural/morphological characterization of Ir/Ru-oxid	de
coatings for neural stimulation electrodes 1	12
8.2 Electrochemical and morphological characterization of Ir/Ru-oxide coatings for	
supercapacitors (SCs)	13
8.3 Electrochemical reduction of CO ₂ in an aqueous electrolyte on Ir/Ru-oxide coatings 1	14
8.4 Direct electrochemical reduction of NAD ⁺ on Ir/Ru-oxide coatings to regenerate 1,4-NAD	ЭН
	14
CHAPTER 9	16
9. Contribution and Future Work1	16
9.1 Contribution to the knowledge	16
9.2 Suggestions for future work	17
REFERENCES1	19

List of Figures

Figure	2.1:	The location of an implanted neural stimulating electrode in relation to the position of neurons
Figure	2.2:	Overview of a neural prostheses <i>(freehand system)</i> 7
Figure	2.3:	An illustration of a basic two-late-capacitor consisting of two conducting metal plates separated by an insulating media 14
Figure	2.4:	Charge and discharge state of EDLC
Figure	2.5:	Overview of the CO_2 reduction reaction pathway as a function of the electrode material
Figure	2.6:	The equilibrium potentials as a function of pH for the principal overall CO_2 reduction reactions (at 25 °C)
Figure	2.7:	Nicotinamide adenine dinucleotide in its oxidized form (NAD ⁺)
Figure	2.8:	Mixed metal oxide (MMO) preparation steps
Figure	4.1:	SEM images of the $Ir_{0.8}$ -Ru _{0.2} -oxide coating (a, b) before and (c, d) after torturing. Images (a, c) present the top-view of the coating surface, while (b, d) represent cross-sectional images of the coatings, illustrating their thickness
Figure	4.2:	Elemental mapping analysis of the $Ir_{0.8}$ -Ru _{0.2} -oxide coating performed (a) before and (b) after torturing

- Figure 7.1: Reduction of NAD^+ to NAD_2 and enzymatically-active 1,4-NADH.R = adenosine diphosphoribose. 102

- Figure 7.5: The percentage recovery of enzymatically active 1,4-NADH produced on an $Ir_{0.8}Ru_{0.2}$ -oxide coated electrode by reduction of 1.0 mM NAD⁺ in a batch electrochemical reactor. 109

List of Tables

Table 2.1:	The effect of anionic species on the faradaic efficiency
Table 6.1:	Infrared band assignments of CO ₂ reduction products adsorbed on an Ir/Ru-
	oxide surface after 8 hours of electrolysis. The wavenumbers refer to
	vibrations presented in Figure 6.7

Nomenclature

AEASA	apparent electrochemically-active surface area (cm ²)
AFM	atomic force microscopy
ATR-FTIR	attenuated total reflectance-Fourier transform infrared
	spectroscopy
С	capacitance (F cm ⁻²)
C_{GA}	areal capacitance (F cm ⁻²)
C_{dl}	double-layer capacitance (F cm ⁻²)
CE	counter electrode
СРЕ	constant phase element ($\Omega^{-1} \text{ s}^{n} \text{ cm}^{-2}$)
CSC	charge storage capacity (C cm ⁻²)
CV	cyclic voltammetry
DSA®	dimensionally stable anodes
E	potential (V)
ECU	external control unit
EDS	energy dispersive spectroscopy
EEC	electrical equivalent circuit
EIS	electrochemical impedance spectroscopy
F	Faraday constant (96485 $C \text{ mol}^{-1}$)
FE-SEM	field emission -scanning electron microscope
FID	flame ionization detector
GC	gas chromatography
GCD	galvanostatic charge/discharge
HER	hydrogen evolution reaction
Ι	current (A)
$Ir-O_X$	iridium oxide
Ir/Ru-O _X	iridium/ruthenium oxide
МО	metal oxide
ММО	mixed metal oxide
MSE	mercury/mercurous sulphate electrode

N	number of moles (moles)
п	exponent of a constant phase element
п	number of electrons
PBS	phosphate buffer saline solution
Q	charge (C)
R	resistance (Ω cm ²)
Ru-Ox	ruthenium oxide
RE	reference electrode
rms	root mean square
SCs	supercapacitance
SEM	scanning electron microscopy
Sr	scan rate (V s ⁻¹)
t	time (minutes)
UV-vis	ultraviolet-visible (spectroscopy)
WE	working electrode
XRD	X-ray diffraction

Further in the text, terms "torturing or activation" will refer to the exposing of Ir/Ru-oxide coatings to prolonged electrochemical cycling in phosphate buffered saline at pH 7.4, within a 5 V potential window.

CHAPTER 1

1. Introduction

Metal-oxide coatings formed on metal substrates (e.g. titanium) have been used in many electrochemistry-based applications, such as in the chloro-alkali industry, particularly, for the production of different valuable chemicals and gases (e.g chlorine, sodium hydroxide, oxygen etc.) [1-3]. In addition, metal-oxide coatings have been employed for other uses such as corrosion protection of metals, production of electrodes for organic synthesis and wastewater treatment. Also, metal-oxide coatings have shown to be good materials for the construction of electrodes for electrochemical supercapacitors (SCs), neural-stimulating electrodes and bio-sensors [1, 3-6]. It has also been shown that these coatings can be used as cathodes for the electrochemical reduction of carbon dioxide to several useful organic molecules, such as ethanol, methanol, formic acid and gases like CH_4 [7-8].

One of the first uses of metal oxide coatings formed on titanium substrates was in the area of chloro-alkali industry for oxygen and chlorine production. The electrodes used in the process are known as Dimensionally Stable Anodes (DSA[®]) [9-14]. These DSAs[®] can be composed of a single metal oxide (MO) or of a mixture of metal oxides, the latter known as mixed metal oxide (MMO) coatings [13]. Surface stability, longer service life, low overpotential and relatively good performance during electrochemical applications make DSAs[®] excellent electrode candidates for many electrochemical applications [13, 15-17].

Many coatings of different metal combinations have been prepared and tested as metal oxide electrodes in various electrochemical applications [3, 14]. Of a particular interest have been metals from the transition group due to their proved good performance in many of the above-mentioned applications [2-3, 13, 16-18]. It was established that metal-oxide coatings produced from a platinum group, namely ruthenium and iridium, compared favourably in certain applications to other metal-oxide coatings [13, 17, 19-20]

In fact, ruthenium-oxide (RuO₂) coatings are widely used in several electrochemical processes, mainly for oxygen/chlorine evolution [9-10, 13], for the construction of SC electrodes [21-25] and for waste water treatment [26-27]. Also, IrO₂ is an active electrode material characterized with wide-spread applications in electrochemical waste water treatment [28], oxygen evolution [29-30], energy storage devices as SCs[4], neural electrodes and sensors [17, 31-33].

However, despite their good performance, these single metal-oxide-based electrodes suffer from some drawbacks. These include delamination of the RuO_2 film from the titanium substrate due to erosion of the surface in acidic media [4, 34-38], loss of current efficiency and surface dissolution [39], low biocompatibility when used as electrodes in neural prosthesis applications [40-43]. Also, with respect to the latter application, IrO_2 entails unstable charge injection performance and unsatisfactory corrosion stability [44-49].

In an attempt to address some of the above-mentioned issues related to the use of pure IrO_2 and RuO_2 coatings, efforts have been made to combine iridium and ruthenium to form bi-metallic iridium-ruthenium oxide (Ir_xRu_{1-x} -oxide) coatings. In fact, this combination is one of the most commonly used class of mixed metal oxide coatings [20, 50]. Iridium-ruthenium based metal oxide coatings have been extensively used as anodes or cathodes in many applications, such as SCs [22, 51], oxygen [29, 52-55] and hydrogen evolution electrodes [37-38], waste water treatment [1, 56-59], in the chloro-alkali industry [9, 56-57] and for cathodic protection against corrosion [60].

Several methods have been adopted to prepare iridium-ruthenium metal oxides coatings [3, 20, 38, 43, 52, 55, 61-64]. Amongst these methods, thermal decomposition is preferred in many applications due to its simplicity and low (processing/production) cost [65]. In thermal decomposition, an inert substrate material (ca. titanium) is coated with a precursor solution containing the desired soluble metals, and then thermally annealed in an oxygen atmosphere to produce the corresponding metal-oxide coating [19].

However, in spite of the significant research that has been done to prepare iridium/ruthenium based metal-oxide coatings through thermal decomposition [2-3, 29, 37, 52, 66], these metal-oxide coatings still face challenges in terms of their

performance consistency [22, 39], practical applicability limitations [38-39, 67] and degradation of the oxide film [38, 46, 64]. In addition, no systematic research on the influence of Ir/Ru-oxide composition on various electrode properties (catalytic activity, stability, charge storage, etc.) have yet been done.

The currently available commercial metal oxide coatings used for neural stimulating electrodes suffer many drawbacks [46, 68]. One of the major problems is their low and irreversible charge storage capacity (CSC). This disadvantage stems from the reduction in the electrode area leading, in many cases, to the failure of the electrode used for neural stimulation [69]. Similarly, the currently available commercial metal-oxide coatings used for supercapacitance (SCs) do not exhibit satisfactory physical/chemical properties which lead, in many cases, to a gradual drop in their capacitance performance with time [4, 22].

This thesis aims at contributing to the area of mixed metal-oxide coatings by developing a bimetallic Ir/Ru-oxide coating on a titanium metal substrate through thermal decomposition. The author makes an attempt to propose solutions to address the above mentioned drawbacks associated with the use of currently available Ir/Ru-oxide coatings.

This coating combination, under experimental condition applied in the current work [70-71], has not been investigated before for neural stimulation electrodes and supercapacitance (SCs). The use of the thermal decomposition method to develop Ir/Ru-oxide coatings is justified by the fact that these coatings are promising electrode materials that are characterized by a high electrical conductivity, significant charge storage, proven capability of adsorbing hydrogen reversibly and elevated electrochemical (corrosion) stability [9, 20, 52, 72].

Along with use of Ir/Ru-oxide coatings for neural stimulation electrodes and supercapacitance (SCs), the author also proposes their use in electrochemical hydrogenation reactions, which is justified by their capability to form metal-hydrogen bonds (Ir-H_{ads} and Ru-H_{ads}) of an intermediate strength [73]. Consequently, the Ir/Ru-oxide coatings developed in current study were used for the electrochemical reduction of carbon dioxide to useful organic molecules [74] and for the electrochemical regeneration of very expensive enzymatic cofactor, nicotinamide adenine dinucleotide 1,4-NADH [75].

CHAPTER 2

2. Background and Literature Review

The following subchapters will present basic information related to four applications of the Ir/Ru-oxide electrode employed in the current PhD project. More specific overview of the same, along with more specific literature references, is given in the Results and Discussion sections of the thesis, which is presented in a manuscript-style manner.

2.1 Iridium-Ruthenium Oxide Coatings as Neural Stimulating Electrodes

2.1.1 Neural prosthetics

Neural prosthetics or neuroprosthetics are a series of devices that can substitute a motor, sensory or cognitive modality that are instrumental in the process of restoring the function of a damaged neuromuscular organ that might have been damaged due to various reasons such as accidents, diseases (like Parkinson's, dystonia, epilepsy, Alzheimer's) or other incidents [76-80]. The field of neural prosthetics deals with the development, designing, fabrication, testing and implantation of artificial body tools or parts as well as reactivation and functioning of human body parts. Common clinical applications of neural prostheses constitute treatment/diagnostic of disease like seizers, epilepsy, migraine, Alzheimer's, dementia [81], restoration of vision, hearing disorders and reduction of pain in the damaged part of the human body [49, 82-87]. Also, they are used for cortical control and spinal cord injury treatment [87-88], deep brain stimulation (DBS, an important treatment for tremor, epilepsy, pain, and Parkinson's disease when pharmacological management is ineffective) [79, 81, 87, 89-90], and devices that restore the mobility and respiration of a paralyzed person [77, 91]. All neural prostheses developed so far have the same basic principle of artificial manipulation of targeted human biological neural system. Artificial manipulation of the neural system is done with an externally induced electrical current to mimic normal sensorimotor functions with the help of an implanted metallic neural electrode, which is used as a bridge between the external electronic control device and the biological system (neurons) [32, 68, 80, 87]. However, each clinical application requires

implantable hardware systems that are specific to the desired function, and therein lay the engineering challenges [87, 92]. If those design obstacles are too be resolved, the development of neural prostheses would be helpful in improving the life of patients suffering from various neurological impairments and diseases [80].

Neural prostheses can be categorized into motor and sensory neural prostheses. Motor prostheses involve treatment of human neuromuscular functions, such as treatment of spinal cord defects, through safe and controlled electrical stimulation. A sensory neural prosthesis is a total replacement of defective neuromuscular activity by means of implanting artificial sensor i.e. cochlear implants [87]. Both for sensory and motor neural prostheses, restoration of the lost neural functions are done with the help of an implanted part, known as neural electrode.

2.1.2 Neural electrodes

An important building block of neural prostheses is the neural electrode that is used for the purpose of stimulating and recording various neural activities. These electrodes are implanted inside the patient's body near targeted nerves tissues, as shown in Figure 2.1.





Basically, the implanted neural electrode enables the transfer of information between an artificial electronic device and the nervous system by acting as a bridge between two different systems, the external electronic control device and the human biological system [68, 80].

There are two types of neural electrodes which are interfaced with the human biological nervous system: (i) *recording* and (ii) *stimulating* electrodes. Recording electrodes typically pick up information from sensory systems, whereas stimulating electrodes often communicate with motor systems [5, 32]. In the context of the current research work, neural stimulating electrodes will be discussed in detail.

2.1.2.1 Neural stimulating electrodes

The neural stimulating electrode is an important component of neural prostheses and plays a vital role in the effective stimulation of nerves. The neural stimulating electrode replaces or treats impaired neuromuscular functioning of a human bodily system or organ, through artificial electrical stimulation [87]. Implanted stimulating electrodes stimulate the nerve cell by transferring electrical current and initiate a functional response by depolarizing the membranes of excitable cells. An action potential is generated due to this excitation in the nerves cells that propagates across the neuromuscular junction to excite the muscle [32, 49]. Depolarization is achieved by the flow of ionic current between two or more electrodes, at least one of which is in close proximity to the target tissue [32]. Stimulation must take place without causing any neural damage inside the body through undesirable reactions such as metal dissolution, oxidation of organics or gas evolution [49].

In order to understand the basic mechanism of neural stimulation, a common neural prosthesis process known as the "freehand system" is shown in Figure 2.2. The freehand neural prosthesis is used for the restoration of hand functions through functional electrical stimulation that helps spinal cord patients control their paralyzed muscles [88, 93].



Figure 2.2: Overview of a neural prostheses (freehand system) [88].

The freehand neural prosthesis (Figure 2.2) consists of metallic stimulating electrodes, an electronic package that drives the electrodes with stimulation currents, and an external component controller that is used to power and control the implanted device. The external components consist of an external control unit (ECU), an induction coil and a shoulder position sensor. ECU with an integrated power source delivers power and sends commands to the implanted stimulator. Stimulator delivers constant-current pulses to neural stimulating electrodes in order to excite nearby neural tissues for patient's hand's grasp operation [88]. Stimulation of nearby neural tissues is done by passing electrical currents in surrounding tissues via neural stimulating electrode. This flow of current causes a voltage drops across the cell membranes of nearby neurons. Within threshold limits, this voltage drop across neuron initiates an action potential that results in activation of a large population of neurons within the vicinity of the implanted neural stimulating electrode [32, 49, 87]. Current flow at the electrode-tissue interface takes place through electrode tip which is the proper site of ionic charge transfer. Both specific nature of the electrode-tissue electrolyte interface and the manner in which charge is transferred across the interface depend on the type of material used for the neural stimulating electrode [87].

Design, fabrication and implantation of neural stimulating electrodes systems are very crucial. Various properties of the neural stimulating electrode like resistance to corrosion, biocompatibility and charge injection capabilities, determine the nature and kinetics of charge transfer between electron conduction in the external circuit and ionic conduction through

electrolytes within the body [94]. An improperly designed neural prosthesis system for neural stimulation may cause damage to nearby human tissues or damage to the neural stimulating electrode itself [5, 49]. Clinical effectiveness and success of neural prosthesis lie in the ability of neural stimulating electrodes to provide a safe level of stimulation without introducing any harmful effects to human health [32].

2.1.2.2 Requirements of materials used for neural stimulating electrodes and challenges

The neural stimulating electrode remains inside the patient's body for a long period of time in order to keep stimulating the neural tissues by passing a suitable amount of charge. The consistency of this stimulation activity for extended periods faces several challenges and requires keen considerations. Several factors should be properly selected for any neural stimulation process. Those include the electrode's proper size, sensitivity of the stimulating probe, reaction of the human tissues, stability of the electrode surface, service time and fouling, to name but a few. Also, controlled and careful stimulation of the excitable neural tissues is the key to success of all neural prostheses. Improper stimulation can induce damage to neural tissues within electrode's vicinity. This damage stems from the overstimulation of the excitable tissues or the toxic electrochemical reactions species injected into the extracellular fluid from the electrode's surface [5]. To achieve safe electrical stimulation of the nervous system, it is necessary to transfer a defined amount of charge from the electrode probe through the neural tissues. This charge injection must be enough and safe to trigger an action potential at a given targeted stimulating spot. Depending upon the type of neural prosthesis and the nature of stimulation for a specific activity, charge injection requirements varies. However, this charge injection process must be reversible without inducing any toxic or unwanted reaction species in the tissue that may have harmful effects [49, 68]. Common irreversible processes encountered with stimulating electrodes during stimulation are water electrolysis, gas evolution, metal dissolution and oxidation of biological organic species present in the human fluids [32]. Employing neural electrodes on micro scale is crucial for implantation. It should be noted that there is direct relationship between the size of the neural electrodes and their charge density during stimulation. The increase in charge density can cause failure of the neural electrode and trigger the production of unwanted species within its vicinity. This is one of the major problems faced by certain neural electrodes that have low and irreversible charge storage capacity (CSC), an important characteristic of the electrode to provide enough charge per pulse during stimulation preventing failure of the neural prosthesis [69]. Also, the attack of the biological fluids such as enzymes and macrophages on electrodes surface is one of the issues which could reduce the stimulation activity of the implants leading to its failure [95]. Due to all the aforementioned concerns and difficulties associated with the stimulating electrodes, and since the life of the patient may hinge upon the choice of the electrode material, the proper selection of the cathode materials and specification is of an extreme importance.

According to previous studies in this domain [5, 94-96], the ideal material for neural stimulating electrode must be (*i*) biocompatible and non toxic for the target tissues, (*ii*) mechanically acceptable for the specific application, (*iii*) strong and flexible enough so that it may not buckle during the implantation as well as during their operation and it must satisfy the service period obligations, (*iv*) capable of delivering sufficient charge, which should be enough to stimulate the targeted tissues, (*iv*) suppressive of any unwanted reaction during electrical stimulation at levels that are toxic to the surrounding tissue, and (*v*) corrosion resistance of the electrode material should be high in order to prevent the premature failure of the electrode.

2.1.2.3 Neural stimulating electrodes materials and charge injection mechanisms

The charge injection capability of neural stimulating electrodes is very important in the selection of an electrode material. For electrical stimulation of neurons, it is necessary to inject a certain amount of charge (10 mC for 1 cm⁻² of electrode surface area) into the membrane of neural tissues [68, 97]. This charge is provided by the neural electrode in close conjunction with the targeted tissues. When this neural stimulating electrode is implanted into the patient's body, an electrode/electrolyte interface is formed. Charge is carried by ions through into the neural tissues [98]. To carry this charge from the electrode to ion flow in the neural tissues, certain reactions are required [32]. These reactions at the electrode/electrolyte interface can be non-faradaic or capacitive in nature, where no electrons are transferred between the electrode and electrolyte. Capacitive or non-faradaic charging of the neural tissues involves charging/discharging of the electrode-electrolyte double layer by means of redistribution of charged chemical species present in the electrolyte. The second mechanism for the charge transfer is due to reversible faradaic reactions, in which charge transfer is done through electrons

transfer between the electrode surface and electrolyte. Charge injection through transfer of electron across the electrode/electrolyte interface is the result of faradaic processes that involve reduction and oxidation reactions. In the faradaic process, species present in the biological solution/electrolyte or electrode's surface are either reduced or oxidized. Faradaic reactions of charge injection are often called pseudocapacitive reactions [5, 32]. However this charge injection process must be reversible and should not harm the surrounding tissue.

A variety of materials have been investigated as neural stimulating electrodes, starting from the noble group metals [32, 99-101] to non metallic biocompatible electrically conductive polymers [102-103] and new emerging materials, like carbon nanotubes [44, 103-104]. It was established that there are certain materials which have the capabilities of charge injection both by capacitive as well as pseudocapacitive charge injection mechanism, e.g. platinum, iridium or their composites [5, 32].

2.1.2.4 Capacitive/non-faradaic charge injection materials

Capacitive electrodes, which inject charge entirely by capacitive charging and discharging of the electrical double-layer, are conceptually attractive because of their minimization of water electrolysis, electrode dissolution, or other irreversible electrochemical reactions that might degrade either the electrode or the surrounding tissue [103, 105-106].

A variety of materials have been used for developing electrodes for neural stimulation applications that undertake stimulation through capacitive mechanism of charge injection. Titanium nitride (TiN) is a potential candidate which is widely used in the making of cardiac pacemaker prostheses due to its biocompatible nature [32, 101, 107-108]. However, lower charge injection limits its use in making microelectrodes for neural stimulation [32]. Tantalum is also one of good electrode materials for neural stimulation that injects charge by a purely capacitive mechanism. Tantalum, in the form of tantalum penta oxide (Ta₂O₅), has been extensively studied and used in several chronic stimulation applications [32, 109-110]. However similarly to the TiN capacitor electrode material, tantalum's low charge injection limits its use for neural stimulation applications. Other issues with this material are the difficulty in achieving adequate electrochemical surface area with regard to its geometrical size and lower bias voltages [32]. Amongst nobel metal group platinum (Pt) has been commonly used as electrode material for

electrical stimulation largely due to its biocompatible nature and high resistance to corrosion. Beside its wide spread use, this material do exhibit some corrosion during electrical stimulation, in addition to possibility of long-term toxic effects on the tissue that stems from the dissolution of the surface. Another issue encountered with Pt, is its soft nature which limits its mechanical strength and restrict its use in certain applications [5].

Another metal from the nobel metal group is gold (Au), which has also been investigated for neural stimulation due to its good resistance to corrosion. However, it has been reported that that oxygen reduction occurs on these gold electrode which generates free radicals known as reactive oxygen species in the tissues. These reaction species have a negative impact on neural tissues [5].

2.1.2.5 Capacitive/faradaic charge injection materials

Capacitive/faradaic charge injection materials inject charge through both reversible faradaic reactions and electrode double layer (non-faradaic/capacitive) charging-discharging [5, 32]. In this way, a higher charge injection can be achieved for stimulations at a micro level extent relative to the electrode size, which might help eliminate the issues related to the purely capacitive electrode materials. As noted previously, amongst several materials used for this purpose, noble metals, such as Pt is widely used in prosthetic devices due to its biocompatible and corrosion resistance nature, however, although there is a short potential region in which the irreversible formation/reduction of Pt-oxide occurs, the maximum charge injection (Qini) limit of Pt is \sim (100-300 μ C cm⁻² geometrical area) [32, 99], which is not sufficient in most cases to stimulate the nerves [100]. Also, dissolution of the surface might occur at low charge densities. Similarly, other well-known electrode materials like silver-silver chloride and stainless steel dissolve at the surface upon exposure to biological tissues, thus causing inflammation [96, 111]. Titanium (Ti) is also a common implantable material due to its non-toxic nature and large thermal/electrical resistance characteristics; however, its low charge injection and UV photo-activity make it unsuitable for neural stimulation and some other medical applications [32, 43, 76, 96, 112]. Ruthenium amongst the various transition metal oxide materials proves to be of the highest performance due to its prominent properties as a pseudocapacitor material and high conductivity. However, its high cost and unproven biocompatible nature limit its use (as pure,

non-alloyed metal) as a commercial stimulating material [40-43]. Rhodium was also studied as stimulating electrode; however its high cost and low biocompatibility limit its use [43]. Some low cost transition metals such as nickel, manganese, cobalt and their composites have also been utilized, but these electrodes are also not adequately biocompatible and corrosion resistive [40, 113-114]. Unlike other pure metals, pure iridium oxide (IrOx) is a popular material for use in neural stimulating electrodes due to its excellent properties such as high reversible charge storage capacity due to the reversible faradaic redox transition ($Ir^{3+} \leftrightarrow Ir^{4+}$) occurring in the oxide phase. This metal oxide has so far been considered as the state-of-the-art neural stimulating electrode [32-33, 44, 47, 115]. However, iridium is brittle, which makes it difficult to develop flexible micro neural electrodes. Also charge injection performance of IrOx electrodes degrade rather rapidly with time due to their unsatisfactory corrosion stability [44-49].

2.1.2.6 New emerging materials

New and emerging materials have been introduced as alternative neural electrode materials. Common advantages of these materials are their flexibility, biocompatibility and wider choice of surface modification for specific neural application [32, 116]. Carbon nanotubes are attractive materials for micro neural stimulation due their high surface area to volume ratio [32, 44, 103-104]. Silicone-based electrode arrays are also widely used in neural prostheses due to their excellent biocompatibility and flexibility; however, deterioration of the surface is observed [116]. Electrically conductive polymers (ECPs) like polyethylenedioxythiophene (PEDOT), polypyrrole and their composites have been investigated as neural electrode materials [32, 103]. However, lower charge injection and poor chemical stability of the polymer materials limit their use for higher current density neural applications [32, 102]. Natural polymers, such as silk, have also been investigated due to their properties closely resembling those of human biological tissues, but due to their brittle nature in dry state, they are very difficult to handle [116-117].

2.1.2.7 Hybrid electrode materials

In an attempt to address some of the above-mentioned issues related to the use of pure electrode material for neural stimulation, efforts have been made to form composite materials that are more stable, biocompatible and capable of achieving higher charge injection. Some of these materials include bi-metallic oxide coatings [118-119], combining conventional electrode

material with emerging materials [44, 120] and novel bilayers polymer composites [121]. However, degradation of the mixed composites at high current pulsing, loss of performance with cycling, brittleness and reproduction in case of polymer mixed materials make these electrodes unsuitable for many clinical uses [5, 99, 121].

In an attempt to address the above-mentioned issues related to electrodes material, this PhD project aimed at developing new bimetallic oxide coatings. These oxide-based coatings would offer higher charge injection and higher surface/volume ratio in comparison to the currently used stimulating electrodes. Iridium was combined with ruthenium in a binary mixture and coated on titanium substrate thermally to form Ir/Ru-oxide coatings. Various physico-chemical properties and surface topography/morphology of bi-metallic iridium/ruthenium-oxide coatings deposited on a Ti substrate were investigated, with the aim of obtaining information that could be useful for their possible future use as neural stimulating electrodes. Ruthenium and iridium were selected as components of the bimetal-oxide electrode due to their high charge storage/injection properties, good electrical conductivity and relatively high electrochemical (corrosion) stability [7-9, 43, 52, 72, 122-126].

Further in the thesis (Chapter 4), it will be shown that the developed Ir/Ru-oxide coatings offer a larger apparent electrochemically-active surface area (AEASA) with high charge storage capacity (up to 27 mC cm⁻²) and a significant corrosion stability even after a prolonged exposure to rather extreme potential-cycling conditions. This can potentially enable a higher degree of miniaturization of neural stimulating electrodes and an increase in charge injection capability, thus making the Ir/Ru-oxide electrodes potentially more biocompatible and functional to be used as neural stimulating electrode material. However, the reader should note that the results presented in this thesis represent only the initial step in future possible development of this electrode material as a neural-stimulating electrode; hence, no attempt has been made to verify the suitability of the material in in-vitro and/or in-vivo systems, which is outlined as a future work.

2.2 Iridium-Ruthenium-oxide Coatings for Supercapacitors

2.2.1 Capacitors

A capacitor is a simple, passive electronic device that has the ability to store energy in the form of an electrical charge. As illustrated in Figure 2.3, a conventional two-plate-capacitor consists of two conducting metal electrode plates separated by an insulating media (known as the dielectric medium) or by vacuum.[127-129].



Figure 2.3: An illustration of a basic two-plate-capacitor consisting of two conducting metal plates separated by an insulating media [129].

The charging process takes place when an external potential difference is applied across the two metal plates which are placed at a given distance and parallel to each other. As both metal plates are separated from each other, a flow of charge between the two plates will not take place, whereas an accumulation of charge will occur on both the plates [130]. Positive charges gradually accumulate on one metal plate while negative charges buildup on the other metal plate [129-130]. When external voltage is applied, charges accumulates on the surfaces of the two metal plates (electrodes) that generates an electric field within the metal plates, known as electrostatic field. The flow of current continues while charging the capacitor making the electrostatic field stronger as it stores more energy. This charge accumulation continues until potential difference across the plates becomes equal to the applied potential. When current flow out of the capacitor, discharging it, the potential difference between the two plates decreases and the strength of the electric field drops [129]

The ratio of the accumulated or stored charge (Q, in Coulombs, C) on the electrode plates to the applied external potential (V, in Volts, V) across them is called the capacitance (C, in Farads, F) of the capacitor [131]:

$$C = \frac{Q}{V} = \epsilon_0 \epsilon_r \frac{A}{d}$$
(2.1)

where ϵ_0 (8.85×10⁻¹² F m⁻¹) is the permittivity of free space, ϵ_r (unitless) is the dielectric constant, A is the active plate (or electrode) surface area and d (meters, m) is the distance between electrode plates. Capacitance is the property of the capacitor which gives the quantity of charge stored on the conductive plates [131], and according to the above equation, it is proportional to the plate surface area and inversely proportional to the separation of the plates.

2.2.2 Supercapacitors (SCs)

Supercapacitors (SCs), also known as 'electrochemical capacitors (ECs)' or 'ultracapacitors' [132-133]. SCs are unique electronic devices that exhibits 20-200 times higher capacitance than conventional electrostatic capacitors [134]. SCs have been extensively investigated due to their high energy-storage densities that can enable them to be used as hybrid capacitors (a capacitor that offers battery-like high energy storage density but can be charged/discharged much faster than batteries) [51, 135-136]. The large capacitance of the SCs stems either from the double-layer capacitance (proportional to the electrode surface area, according to Equation (2.1)), pseudocapacitance associated with surface redox-type reactions or the combination of both [134]. SCs have the potential to provide short-duration power bursts, and they are having life cycles up to several millions, which is much higher than what batteries offer (up to 1000) [137]. Other worth mentioning characteristics of the SCs include their excellent charge/discharge cycling stability and high power supply, which make them important devices for energy storage [132-133]. The higher capacitance value (per unit mass or volume) for SCs can be attributed to: (i) the significantly small distance through which charge separation takes place in the electrochemical double layer (EDL) that is formed at the electrode/electrolyte interface, (ii) the large surface area of the electrode that stems from the presence of a high number of pores in the electrode material, and (iii) the facility of the energy storage mechanism that consists of the ion movement in between the electrode surfaces [4]

2.2.2.1 Types of Supercapacitors

Supercapacitors are categorized into two basic groups on the basis of electrochemical response and energy storage mechanism: (i) *electrochemical double layer (EDLC) capacitors*, and (ii) *pseudo-capacitors*. With regard to EDLCs, electrical charge is accumulated at the electrode/electrolyte interface (double layer) exposed to the electrolyte and hence capacitance comes solely from the charging/discharging of the electrolyte double layer by means of redistribution of charged chemical species present in the electrolyte [4, 132]. The corresponding capacitance obeys Equation (2.1). To better understand this charging and discharging mechanism of the SC, Figure 2.4 presents a carbon-based SC, which is one of the most common electrochemical EDLC materials [138].



Figure 2.4: Charge and discharge state of EDLC [139].

As can be seen in Figure 2.4, the SC consists of two electrodes (C_1 and C_2) with an electrolyte functioning as separator in between them. As mentioned earlier, when an external potential difference is applied across the two plates, the charging process of the capacitors starts [130]. The charged surface of the electrodes attracts ions of opposite charge in the electrolyte;

positive charges gradually accumulate on one electrode while the negative charges accumulate on the other electrode surface thus forming the electrical double layers (EDL) at the electrode/electrolyte interface [129-130]. Each electrode (C_1 and C_2) behaves individually as EDLC, while the system represents two capacitors in a series [139]. The double layer capacitance, C_{dl} , at each electrode interface can be calculated from Equation (2.1).

The maximum energy stored, E (Joules, J) and power delivered, P (Watts, W), of SC are calculated from [4, 132]:

$$\mathbf{E} = \frac{1}{2} \, \mathbf{C} \mathbf{V}^2 \tag{2.2}$$

$$P = \frac{V^2}{4R}$$
(2.3)

where V (volts, V) is the operating voltage and R (ohm, Ω) is the equivalent series resistance (ESR). Therefore in EDLCs, capacitance is strongly dependent on the surface area of the electrode materials that is exposed and accessible to the electrolyte ions. Large surface area activated carbon is one of the best examples of a double layer capacitor material [138].

The other category of the SCs is the pseudo-capacitors in which fast and reversible faradic processes (redox reactions) take place on the surface of electrode material [132]. The principle behind pseudocapacitance-based SC was firstly developed by Conway et al [133]. Pseudocapacitance arises from the faradaic currents of couple electrochemical reactions [137].

Pseudocapacitance plays an important role in developing high energy storage SCs, however, a very thin surface layer is utilized in achieving capacitance during these faradic surface redox reactions that hinder their wide spread applications as electrode materials. Similarly, the poor electrical conductivity and degradation of the materials used for EDLCs limit their use. Effective utilization of the maximum surface of the electrode materials and enhanced resistance can be achieved using hybrid SCs. These hybrid SCs include several composite materials that not only increase the capacitance of the SC but also improve its conductivity, surface utilization and resistance to corrosion [132]. Hybrid SC combines features of the two SC conventional models and typically exhibit better capacitive behavior than in practiced EDLC and pseudocapacitor. Metal oxide coatings (e.g. RuO₂/Ti, RuO₂/CNT (carbon nano tubes)) are most
common hybrid SCs materials [51, 132]. Hybrid pseudo-capacitor materials posses several oxidation states and store energy not only through the charging of the electrochemical double layer, but also through reversible redox reactions occurring on or near the electrode surface and in the bulk of the solid material close to the solid/liquid interface[51]. This means that an additional charge can be stored/delivered.

2.2.2.2 Material used for supercapacitors (SCs)

Several materials have been researched as electrodes for SCs along with the most traditional carbon and carbon-derived materials. SCs based on carbon and carbon derivatives, like graphite, glassy carbon, carbon nanotubes (CNTs), graphene, activated carbon, carbon fibers (CFs), [132-133, 138, 140-142], conductive polymers [135] and various pure or hybrid metal oxides [4, 51, 136, 143] are the most noteworthy. Amongst the aforementioned employed materials for SCs, pure metal oxide (MO) or mixed metal oxide (MMO) is of a special interest. MMOs for SCs have been extensively investigated due to their potentially high energy-storage densities that can enable them to be used as hybrid capacitors [135]. An important advantage that MMOs offer in comparison to traditional EDLCs is the additional charge that can be stored/delivered through reversible faradaic process (redox reactions) occurring in the solid phase close to the electrode surface [51]. Thus, the EDL effect is combined with a faradaic process resulting in higher capacitance [137].

Transition metals and their oxide coatings based supercapacitors have recently attracted significant attention due to enriched redox activities and promising capacitance performance. Coating materials include RuO₂, IrO₂, MnO₂, CoO₂, NiO₂, FeO₂, SnO₂ and CuO₂ [4, 137]. However, certain MOs still suffer from some drawbacks including the loss of catalytic activity, detachment of the oxide film resulting in lower capacitance and high electrolyte resistance [34, 135, 144-146].

Despite the abovementioned flaws encountered with MOs, ruthenium oxide (RuO₂) proves to be one of the most promising candidates for SCs with a large specific capacitance (C_{sp} ; theoretically reaching 1358 F g⁻¹) [147]. Other distinguishable properties of RuO₂ like high conductivity, wide double layer region and redox reversibility make it highly attractive material for SC electrode materials [21-25]. This was emphasized by many research groups that have reported large capacitance values for RuO₂; however the method of preparation and experimental conditions used, played a role in the level of performance [4, 24]. Despite its proven performance, the use of RuO₂ is associated some drawbacks; for example, oxide delamination due to erosion of the surface in acidic media and loss of capacitance [4, 34-36]. To address these issues and to further improve the performance and stability of the RuO₂, many researchers have relied on composite SC electrodes containing RuO₂ mixed with other metal oxides, such as: RuO₂/SnO₂ [148], RuO₂/NiO, RuO₂/Ta₂O₅, RuO₂/Pt [149], RuO₂/TiO₂, RuO₂/MoO₃, RuO₂/CaO and RuO₂/V₂O₄ [4] and hybrid RuO₂ with carbonaceous materials [150-152].

A promising hybrid metal oxide material for SCs can be achieved by combining ruthenium with iridium in a bimetallic Ir/Ru-oxide electrode. Iridium is characterized with high electrochemical (corrosion) stability in acidic medium [9, 123, 153]. The combination of iridium and RuO₂ to form a mixed metal oxide (MMO) was proven to increase the stability of RuO₂ [9, 123]. Hu et al. [22, 51] have developed a hybrid two-dimensional Ir/Ru-oxide material by applying a one-step cyclic voltammetric deposition (CVD) method yielding a relatively large areal capacitance (C_{GA}, nearing 65 F cm⁻²). However, these bimetallic electrodes showed an undesirable decrease in capacitance after galvanostatic charge/discharge (GCD) cycling and cyclic voltammetry (CV) cycling in acidic media [22, 51].

In an attempt to develop new SCs electrode material that would address some of the abovementioned problems associated with pure RuO₂ and Ir/Ru-oxide composite MMOs, we have developed a new bimetallic iridium ruthenium oxide coating through thermal decomposition; to the best of the thesis author's knowledge, the use of this MMO for SCs has not been reported in the literature by others. As noted previously, ruthenium and iridium were selected as components for the bimetal-oxide electrode because their thermally-formed oxides are promising due to their good electrical conductivity and relatively high electrochemical (corrosion) stability [7, 9, 43, 52, 72, 122]. These oxide-based coatings are thought to offer a relatively higher areal capacitance (C_{GA} , F cm⁻²) and good stability in comparison to the currently used RuO₂ and Ir/Ru based SC electrodes.

Various physico-chemical properties and surface topography/morphology of bi-metallic iridium/ruthenium-oxide coatings deposited on a Ti substrate were investigated, with the aim of obtaining information that could be useful for their possible future use as SC electrode material.

Further in the thesis (Chapter 5), results on the investigation of performance of Ir/Ru-oxide coatings for SCs electrode material will be discussed in details. It will be shown that the addition of IrO_2 to RuO_2 improved the stability and capacitive performance of the thermally prepared Ir-Ru-oxide coatings. The developed Ir/Ru-oxide coatings proved to offer a good areal capacitance values (C_{GA} , 85 mF cm²) and an apparent stability even after a prolonged exposure to rather extreme potential-cycling conditions, i.e. within the potential window of 5 V in a chloride-containing corrosive electrolyte.

2.3 Iridium-Ruthenium-oxide Coatings for the Electrochemical Reduction of CO₂

2.3.1 Overview

The rise in CO_2 emissions has been the center of attention for many years due to the great risks that the mounting CO_2 levels pose on the people and the environment. Over the 20th century, the atmospheric concentration of key greenhouse gases has gone up primarily due to human activities according to the United Nations Framework Convention on Climate Change [154]. Of a particular concern is a CO_2 emission due to its primary role in the irreversible climate change that poses threats including the increase in the temperature of the earth's surface, the possible collapse of the ice sheet and the increasing acidity of ocean water [154]. Hence, these alarming facts necessitate seeking methods to either curb the rising levels of emissions or reduce the concentration of CO_2 in the atmosphere.

There are several methods sought by scientists and engineers to address the rise in CO_2 emissions in attempt to mitigate their negative impact. In spite of the rise in the use of CO_2 capturing and sequestering techniques in the previous decade, those techniques proved to suffer from drawbacks such as the high cost of CO_2 capture, separation, purification and transportation to user sites [155]. That is why another approach which involves converting CO_2 into useful low carbon fuels or organic molecules has been considered.

The conversion of CO_2 to value-added products can be achieved by chemical, photocatalytic and/or electrochemical pathways [156-157]. Electrochemical reduction seems to be a more attractive and promising route when either surplus electricity is available or low-cost

electricity (e.g, like in Quebec, Canada). It can be performed at ambient temperature and pressure, in the presence or absence of light. In addition, the experimental setup is relatively simple and therefore highly controllable and can achieve high conversion efficiencies making it viable economically for industrial scale-up and practicability [158]. Also, the power needed to drive the reaction can be obtained without generating any new CO_2 through the use of sustainable routes such as solar, wind, hydroelectric or geothermal energy supplies [158]. Another advantage of using electrochemical reduction is the ability to fully recycle supporting electrolyte so that the overall consumption can be minimized to simply water or wastewater [158].

2.3.2 Electrode material for CO₂ reduction

One of the major challenges that face scientists in the field of electro-reduction of CO_2 to useful products is the ascertainment of the reaction mechanism by which the reaction occurs [159]. The complexity lies in the selectivity of different metals or group of metals towards different products with varying efficiencies. Although there have been many proposed pathways for a specific product distribution, it has been generally agreed upon that the first intermediate in the process is the formation of CO_2 ⁻⁻ radical [155, 160]. This intermediate is very unstable and reacts readily either with water molecules, hydrogen ions or other molecules present in the electrolyte, including CO_2 [155]. The formation of CO_2^{--} is the rate determining step in the electrochemical reduction of CO_2 [155, 158, 160-162]. Metals that provide a stable anchor for CO_2^{--} (i.e. strongly adsorb the radical) are likely to achieve a high and efficient rate of CO_2 reduction [155]. Hence, the stability of the intermediate at the electrode is a key factor to consider in assessing any reaction mechanisms.

Since different metal electrode can bind to the first CO_2 electro-reduction intermediate to varying degrees, those electrodes can be classified into three categories based on (i) their final products (ii) tendency to bind to CO_2 ⁻⁻ and (iii) hydrogen overpotential [155, 160]. Metal groups that have a weak tendency to adsorb CO_2 ⁻⁻ give formate as major product. This group includes Pb, Hg, In, Sn, Cd that also exhibit high hydrogen overvoltage [155, 160]. The 2nd group, which include Au, Ag, Zn, Pd, Ga, Fe, Co, Cu, and Ni, bind CO_2 ⁻⁻ to varying degrees, and CO is usually the typical CO₂ reduction product encountered with these kinds of metals. The only exception is

Cu which exhibits the highest catalytic activity for the production of hydrocarbons, alcohols, and aldehydes [155, 160]. However, Cu requires overpotential of almost 1 V and the reaction does not proceed with high selectivity as fairly broad mix of major and minor products are produced [163-164]. Despite the low selectivity and high overpotential, Cu is the only known metal capable of catalyzing the formation of significant amounts of hydrocarbons at high reaction rates over sustained periods of time. For the third group of metals, such as Ti, V, Nb, Ta, Cr, Mo,W, faradaic efficiencies for the evolution of hydrogen (H₂) are approximately 100% due to the significant bond strength between the catalyst and the hydrogen ions and thus, these materials are not suitable as good CO₂ reduction electrocatalysts [163-164].

Figure 2.5 shows the formation of various CO_2 reduction products according to the coordination state of CO_2 and the electrode material. It should be noted that Figure 2.5 does not include all the intermediate steps for a desired product due to the lack of data in this regard.



Figure 2.5: Overview of the CO_2 reduction reaction pathway as a function of the electrode material [155].

This simplified scheme indicates that following the formation of the first intermediate to which the affinity of binding is determined by the nature of the metal electrode used, the next intermediate is essential in determining the path through which CO_2 reduction takes place. If CO is formed on the electrode then this intermediate can be further reduced under the favorable process conditions, each of which will be discussed later. Formats on the other hand are stable products that cannot be further reduced. Only Cu exhibits a proven ability to produce hydrocarbons and alcohol through the reduction of CO in the presence of hydrogen ions. Although the nature of the catalyst is an important factor in determining the product distribution, efficiency and selectivity of the process, other process factors (e.g pressure, temperature, and pH) are also influential in the electro-reduction of CO_2 to usable products.

2.3.3 Governing factors of the CO₂ reduction reaction

Extensive research in the field of CO_2 electroreduction provides a detailed overview about the importance of process conditions for obtaining the desirable performance. It was reported that the product distribution, selectivity, and faradaic efficiency is dependent on factors such as electrode, pressure, temperature, supporting electrolyte, pH and the interplay among these parameters governs the performance of the process [155, 159, 165-166]. The faradaic efficiency describes the percentage of electrons that end up in forming the desired product and it is used as in many electrochemical applications to assess the performance and the selectivity of the process [166].

2.3.3.1 Effects of supporting electrolytes

The electrolyte has a significant role in electrochemical reduction of CO_2 . A number of prior reports have shown that the electrolyte choice has profound effects on current density, product selectivity, and faradaic efficiency in CO_2 reduction [155, 159, 164, 166]. In general, the choice of the supporting electrolyte is vital in electrochemical processes in attempt to increase the conductivity of the solution and eliminate the transport of electroactive species by ion migration in the electric field, to maintain ionic strength and to control pH. Conventionally,

electrolytes implemented in electrochemistry are categorized by their phases, aqueous and nonaqueous, which are discussed below.

An aqueous electrolyte is usually a solution in which ions are dissolved in water [155]. The reason behind using this electrolyte is abundance of hydrogen ions in the media which are part of the CO_2 reduction mechanism [158]. However, two major issues usually limits the use of aqueous electrolyte, including the lack of solubility of CO_2 reduction at ambient pressure and temperature [155], and the fact that the competing hydrogen evolution reaction is more favorable in this system due to the abundance of hydrogen ions [155, 158-160].

A nonaqueous electrolyte, on the other hand, is justified due to its ability to suppress the competing HER (hydrogen evolution reaction) that takes place otherwise in aqueous medium [158, 160]. Typically, one expects to utilize the non-aqueous system to minimize the competing HER and to increase the solubility of CO_2 , compared with that in water. Methanol, for example, dissolves more than 4 times as much CO_2 at ambient conditions than water, therefore a non-aqueous solvent can be thought as an alternative to using high pressure [158, 160, 167]. One of the major hurdles that limit the use of non-aqueous systems for CO_2 reduction is cost, since the vast majority of non-aqueous solvents are much more expensive than water itself, especially if one uses ionic liquids [158, 160, 167]. This lowers the efficiency of the process and decreases the likelihood of its practical applicability.

The importance of the electrolyte does not only lie in the nature of solvent used but it also extends to the type of the cationic and the anionic species. It was reported that changing the cationic species of the electrolyte while holding all the experimental conditions constant can lead to a change in the product distribution and the efficiency [160]. For example, Hori et al. [160] reported that the cation choice (i.e. Li+, Na⁺, K⁺, and Cs⁺) for bicarbonate (HCO₃⁻) electrolytes significantly impacts the distribution of CO₂ reduction products formed on copper electrodes. It was hypothesized that the cation size plays an important role in CO₂ reduction [160]. It was reported that larger cations favor CO production and suppress HER [168].

Kenis et al. [169] also investigated the influence of electrolyte composition on the electrochemical reduction of CO_2 to CO in an electrochemical flow reactor. Similar to the conclusions of Hori et al. [160], it was reported that the presence of large cations such as Cs^+

enhances the performance of the process by improving the partial current density for CO production. In addition, the conclusions indicated that the presence of large cations suppresses HER leading to an increase in the faradaic efficiency of CO_2 reduction process.

Hori et al.[160] also reported that anion choice (e.g Cl⁻, ClO₄⁻, SO₄⁻, HCO₃⁻, H₂PO₄⁻), each with different buffer capacities, influences the local pH at the Cu electrode and thus the nature and the amount of products formed. This aspect will be elaborated in the following section.

2.3.3.2 The effect of pH

 CO_2 electrolysis has been performed in acidic, neutral, and basic conditions, according to the desired final product. The pH conditions in the reactor directly influence the reaction rate of CO_2 reduction [160, 164]. This is due to the presence of a competing hydrogen evolution reaction that depends on the presence of hydrogen ion in the solution. The effect of pH is manifested in Figure 2.6, which shows the shift in equilibrium potential for several reactions on a copper electrode [170].



Figure 2.6: The equilibrium potentials as a function of pH for the principal overall CO_2 reduction reactions (at 25 °C) [170].

The general trend is that with an increase in pH, the equilibrium potential decreases almost at the same slope for all the electroactive species present in Figure 2.6. It should be noted that Figure 2.6 describes the reactions only from a thermodynamic aspect. While, thermodynamically, methane and ethylene should occur at a less cathodic potential than hydrogen, kinetically this does not occur [170]. In addition, the pH in the system is not solely

determined by the composition of the electrolyte. The bicarbonate buffering system is also an important aspect to consider. Indeed, one of the many challenges in electrochemical CO_2 reduction chemistry is related to the interaction between CO_2 and water [155]. The introduction of CO_2 into an aqueous solvent entails a complex series of reversible reactions as shown in reactions 2.1 and 2.2.

In the CO₂ and bicarbonate system, the key equilibria are:

$$CO_2+H_2O \leftrightarrow (H_2CO_3) \leftrightarrow HCO_3^- + H^+ \quad pKa=6.4$$
 (2.1)

$$HCO_3^- \leftrightarrow CO_3^{-2^-} + H^+$$
 pKa= 10.3 (2.2)

In CO₂ saturated bicarbonate solutions, the equilibrium concentration of H_2CO_3 is very low and the kinetics of its formation is slow. Thus near the electrode surface where the hydroxide is forming, most of the buffer capacity stems from reaction 2.2 which has a much higher Ka and thus can result in a significantly higher local pH. Hence, in case a solution that does not exhibit buffering capability is used, such as KCl or H_2SO_4 , one would expect to have a higher local pH at the electrode/electrolyte interface. This effect is presented in Table (2.1)

 Table 2.1: The effect of anionic species on the faradaic efficiency [160].

				-			•					
Solution	Conc.	pH ^a	Potential	Faradaic efficiency (%)								
	Μ		V vs.SHE	CH_4	C_2H_4	EtOH	PrOH	CO	HCOO	H_2	Total	
KHCO3	0.1	6.8	-1.41	29.4	30.1	6.9	3.0	2.0	9.7	10.9	92.0	
KC1	0.1	5.9	-1.44	11.5	47.8	21.9	3.6	2.5	6.6	5.9	99.8	
KC1	0.5		-1.39	14.5	38.2	Ь	Ь	3.0	17.9	12.5		
$KClO_4$	0.1	5.9	-1.40	10.2	48.1	15.5	4.2	2.4	8.9	6.7	96.0	
K_2SO_4	0.1	5.8	-1.40	12.3	46.0	18.2	4.0	2.1	8.1	8.7	99.4	
K_2HPO_4	0.1	6.5	-1.23	17.0	1.8	0.7	tr	1.3	5.3	72.4	98.5	
K_2HPO_4	0.5	7.0	-1.17	6.6	1.0	0.6	0.0	1.0	4.2	83.3	96.7	

^apH values were measured for bulk solution after electrolysis.

'Not analyzed

As shown in Table 2.1, a non-buffered electrolyte, like KCl, KClO₄, does not alleviate the increase in pH at the electrode/electrolyte interface. That is the reason why the hydrogen evolution reaction is suppressed using these electrolytes. On the other hand, it can be seen that the hydrogen efficiency is high upon using the buffer solution K_2 HPO₄ that exhibits a Ka of

around 6.2. The other buffer solution $KHCO_3$ has a Ka of 10.3 which leads to the suppression of the undesired hydrogen evolution reaction.

2.3.3.3 Temperature

Temperature is one of the main factors that influence the performance of CO_2 electroreduction. This influence is related to the correlation that exists between solubility of gases in solutions and the temperature of the system, which is generally an inversely-proportional correlation [155, 162].

The effect of temperature on the electrochemical reduction reaction of CO₂ has been studied by several researchers. Azuma et al.[162] have reported that upon lowering the temperature to 2°C, the reduction efficiency increased dramatically on Ni electrode using a KHCO₃ electrolyte in an aqueous solution in comparison to room temperature where the hydrogen evolution reaction is predominant. It was mentioned that CH₄, C₂H₄ and C₂H₆ are detected for all metal electrodes used in the study despite the inactivity that some of those metals exhibit in CO₂ electroreduction at ambient conditions. The higher reduction efficiencies obtained was attributed to the increased solubility of CO₂ and the increased stability of the reduction intermediates at low temperature. Jitaru et al.[171] also studied the effect of temperature on the electroreduction of carbon dioxide to formate on bronze electrode. The results showed a linear rise in current efficiency to a value of 74% at 12 °C compared to around 59% at room temperature. Cabrera et al. [172] conducted electrolysis in a CO₂ saturated medium using Cu as working electrodes and KHCO₃ as a supporting electrolyte in an aqueous solution. The linear sweep voltammetry employed in the experiment showed that the CO₂ reduction peak current increased with increased temperature despite the drop in solubility. This aspect was linked to the presence of another rate determine step which is the dissociation of CO or its reduction to give higher order products.

2.3.3.4 Pressure

Similar to the effect of temperature, pressure is also an important factor to consider in the electro-reduction of CO_2 . Several workers studied the effect of pressure on the selectivity, efficiency and the product distribution of CO_2 reduction on a metal or set of metal electrodes.

Hara et al. [173] investigated the effect of elevated pressure on various electrodes galvanostatically at large current densities in aqueous KHCO₃. It was proposed, on the basis of the comparison of electrocatalytic activities at CO₂ pressures of 30 atm and 1 atm, that metal electrodes can be classified into four groups depending upon the effect of pressure: the first group includes Ti, Nb, Ta, Mo, Mn, and Al which does not encounter any change of selectivity following the rise in pressure as hydrogen is the dominant product at ambient and high temperature. The second group contained Zr, Cr, W, Fe, Co, Rh, Ir, Ni, Pd, Pt, C and Si for which the process selectivity is altered since formic acid and CO form with high efficiencies at CO_2 pressure of 30 atm whereas hydrogen is the major product at ambient conditions. The third group includes Ag, Au, Zn, In, Sn, Pb and Bi which form CO and formic acid at both ambient and high pressure. The fourth group includes only Cu whose selectivity depends on the CO₂ pressure and the current density. Ito and his coworkers employed an elevated pressure up to 20 atm for the electrochemical reduction of CO_2 in aqueous and non-aqueous solutions [164]. It was indicated that the current density of the reaction rises relative to ambient conditions. Hori et al.[160] also reported on the effect of pressure on the electro-reduction of CO₂; it was concluded that the elevating the pressure alters the current density, the efficiency and the selectivity of some products.

As a result, it can be concluded that pressure is an important element in the process of electroreducing CO_2 since it triggers a change in the performance in the regard of either, efficiency, selectivity or product distribution.

In conclusion: Despite the interesting prospects of CO_2 electroreduction, some challenges still hinder the commercial applicability of the process. These include the slow kinetics of the CO_2 reduction reaction either due to the low activity of the electrocatalyst, or the affinity of the electrode to the competing hydrogen evolution, the latter largely influencing the CO_2 reduction efficiency [158-160]. Electrocatalysts are a vital building block of the process since they bind and activate CO_2 in order to reduce the high overpotentials typically encountered [174]. Also, electrocatalysts can drive selective formation of desired products. In the past decade, the use of bare metallic electrode was the focus of many researchers [160]. However, the low activity of many of the previously employed electrocatalyst and their high overpotentials for CO_2 reduction lowered the favorability of the process and necessitated seeking new electrocatalysts of higher activity. Therefore, in attempt to optimize the process of CO_2 electroreduction, it is vital to develop an electrode material than can present a solution to the low activity encountered with many of the current electrodes while maintaining a high selectivity and faradaic efficiency.

Further in this thesis (Chapter 6), it will be shown that iridium-ruthenium metal oxide coatings prove to achieve a remarkable performance with regard to CO_2 reduction by attaining a faradaic efficiency of 96% and product selectivity toward organic molecules in an aqueous solution.

2.4 Electrochemical Reduction of NAD⁺ to enzymatically-active 1,4-NADH

2.4.1 Coenzyme nicotinamide adenine dinucleotide, NAD(H)

Nicotinamide adenine dinucleotide (Figure 2.7) is a coenzyme used in several hundred biochemical reactions catalyzed by redox enzymes. The main function of the coenzyme in these biochemical reactions is to transfer electron and hydrogen (see Reaction 7.1 on page 101). Hence, the NAD(H) is found in two forms; in an oxidized, NAD⁺, and in a reduced, 1,4-NADH form. Due to the industrial and biomedical importance of 1,4-NADH, and also due to its very high price (for example, 100 mg of α -nicotinamide adenine dinucleotide, reduced disodium salt, from Sigma Aldrich is priced at \$1,150 per 100mg for >90% purity, which translates to \$11.5millions/kg, Cat.# N6879-100MG), the electrochemical regeneration of 1,4-NADH is of particular interest in the field of enzymatic biocatalysis, especially due to the fact that the coenzyme is required at stoichiometric quantities.



Figure 2.7: Nicotinamide adenine dinucleotide in its oxidized form (NAD⁺).

2.4.2 Regeneration of 1,4-NADH

In order to regenerate enzymatically-active 1,4-NADH, various methods such as enzymatic, electrochemical, chemical and photochemical and biological, have been employed in the past [175]. Among them, the electrochemical method offers one of the best approaches due to the fact that the reducing agent is electrons, rather than a chemical, which simplifies the process and eliminates the problem of isolation (separation) of 1,4-NADH. However, a problem that arises in the electrochemical reduction of NAD⁺ on bare (unmodified) electrodes is the predominant formation of an enzymatically-inactive NAD₂ dimer, which is due to the slow kinetics of the second electron transfer and hydrogenation. For example, literature shows that the yield of enzymatically-active 1,4-NADH (relative to the amount of inactive NADH isomers and the NAD₂ dimer) produced on a platinum electrode ranges from 30 to 50% [176-178] and on mercury it ranges from 10 to 76% [179-184]. A tin-oxide electrode yielded 10% of enzymatically active 1,4-NADH [185], and on a reticulated vitreous carbon electrode the yield was only 0.6 % [186], while on gold-amalgam it was 10 % [176].

To obtain higher yields of enzymatically-active 1,4-NADH, many research groups have developed 'surface-modified' electrodes [176, 187-191]. However, certain problems are associated with these electrodes such as high cost and low stability for prolonged use, which limits its applicability at the industrial scale.

To address the above mentioned problems, an Ir/Ru-oxide coating formed on a titanium substrate was employed in this work as a cathode for the electrochemical reduction of NAD⁺ to enzymatically-active 1,4-NADH. The rationale for choosing Ir and Ru was based on the fact that both metals are good hydrogen evolution catalysts due to the optimum metal hydrogen bond strength [29], thus enabling the formation of 'active' hydrogen at low cathodic potentials and its subsequent release for the (electrochemical) hydrogenation of NAD-radical, thus minimizing the formation of inactive dimer, NAD₂ (see Figure 7.1 on page 101).

Further in the thesis (Chapter 7), it will be shown that the Ir/Ru-oxide cathode is highly electrocatalytically-active in producing enzymatically-active 1,4-NADH, enabling a 88% recovery (the percentage of 1,4-NADH in the product mixture). To the best of author's

knowledge, this is the first report on the use of Ir/Ru-oxide electrode for the electrochemical reduction of NAD⁺ to enzymatically-active 1,4-NADH.

2.5 Mixed Metal-Oxide Coatings (MMO)

As it is clear from the text presented so far in the thesis, the current PhD project was based on the use of an Ir/Ru-oxide electrode (i.e. a mixed metal-oxide (MMO) electrode) in four major areas: (i) charge delivery for neural stimulation, (ii) charge storage/delivery for energy management, (iii) electrochemical conversion of CO₂ to useful organic molecules, and (iv) electrochemical regeneration of 1,4-NADH. While the first two applications are based on the capability of the Ir/Ru-oxide coating to offer reversible redox transitions in the solid phase, the last two applications are based on the capability of the electrode to efficiently catalyse electroreduction reactions based on hydrogenation. The following text will present basic general information on metal-oxide coatings used for electrochemical purposes.

The introduction part of the thesis presented some basic information on metal-oxide coatings used for electrochemical purposes.

Mixed metal-oxide (MMO) coatings are made of multiple metal oxide layers on the same substrate, from several precursors, with the goal of improving the oxide material performance taking advantages of the good properties of individual precursor constituents [192]. MMO coatings have been used as anodes in many electrochemistry-based applications, such as the chloro-alkali industry, particularly, for the production of different valuable chemicals and gases (e.g chlorine, sodium hydroxide, oxygen etc.) [1-3]. Various MMOs have also been investigated for organic synthesis, wastewater treatment and electrode material for SCs and neural-stimulating electrodes [1, 3-6, 193]. It has also been shown that these MMO coatings can be used as cathodes for several electrochemical applications such as the electrochemical reduction of carbon dioxide [7-8].

Several methods have been adopted to prepare metal oxide coatings [3, 38, 43, 52, 55, 61-64]. Amongst these methods, thermal decomposition is preferred in many applications due to its simplicity and low (processing/production) cost [65].

2.5.1 Development of mixed metal-oxide coatings (MMO) through thermal decomposition

In thermal decomposition, an inert substrate material (ca. titanium) is coated with a precursor solution containing the desired soluble metals, and then thermally annealed in the presence of oxygen to produce the desired metal-oxide coating [19]. Figure 2.8 demonstrates a simplified scheme which illustrates the major steps in developing metal-oxide coatings through thermal decomposition.



Figure 2.8: Mixed metal oxide (MMO) preparation steps.

Oxidation of the metals in the applied precursor salt is done at elevated temperatures, usually ranging from 200 to 600 °C. Subsequent application of new metal-precursor layers (i.e. coating layers) on the substrate surface is maintained until the desired metal oxide layer thickness is achieved [11, 19, 118, 194-195].

2.5.1.2 Metal-oxide coating electrodes

Conductive metal oxide coatings have been of high technological importance since 1960s [12, 196]. Metal-oxide coatings significantly enhance the electrochemical and surface properties of the electrode system by providing (i) surface stability, (ii) prolonged service life, (iii) improved electrocatalytic activities, and (iv) optimum operating voltages for certain applications [10-11, 55, 64, 197]. The aforementioned characteristics make MMO coatings an attractive electrode material for researcher in various applications. The proper selection of the substrate and coating materials play an important role in achieving the desirable performance.

Many coatings of different metal combinations have been prepared and tested as metal oxide electrodes in various electrochemical applications [3, 14]. Of a particular interest have

been metals from the transition group [2-3, 13, 16-18]. Many combinations of oxides of the platinum group metals were investigated, amongst which IrO₂/TiO₂, RuO₂/TiO₂, TiO₂/RuO₂/IrO₂, ZrO₂, TiO₂/RuO₂/SnO₂ and TaO₂/IrO₂ are the most common and commercially available MMO materials [194, 196]. It was established that MMO coatings produced from a platinum group, namely ruthenium and iridium, compared favourably in certain applications to other metal-oxide coatings [13, 17, 19-20]. In fact, oxide coatings of ruthenium and iridium are widely used in several electrochemical processes. RuO₂ is extensively used for oxygen/chlorine evolution [9-10, 13], for the construction of SC electrodes [21-25] and for waste water treatment [26-27]. Also, IrO₂ is an active electrode material characterized with wide-spread applications in electrochemical waste water treatment [28], oxygen evolution [29-30], energy storage devices as SCs [4], neural electrodes and sensors[17, 31-33].

Despite their good performance, these single metal-oxide-based electrodes suffer some drawbacks. These include delamination of the RuO₂ film from the titanium substrate due to erosion of the surface in acidic media [4, 34-36, 198], loss of current efficiency and surface dissolution [39], and low biocompatibility when used as electrodes in neural prosthesis applications, [40-43]. Also, with respect to the latter application, IrO₂ entails unstable charge injection performance and unsatisfactory corrosion stability in certain applications [44-49]. Extensive studies have been made to address these issues with the use of pure IrO₂ and RuO₂ coatings. In these efforts, iridium was combined with ruthenium to form bi-metallic iridium-ruthenium oxide (Ir_xRu_{1-x}-oxide) coatings. Combining iridium with ruthenium significantly improved performance of both materials with regard to corrosion resistance and long term stability. Due to the superior performance of this coating combination, it has become one of the most used MMO electrode coating materials for a broad range of applications [20, 50].

In order to investigate the superior properties of iridium-ruthenium oxide coatings, this material was considered in this PhD project for several novel applications in electrochemistry including (i) neural stimulating electrodes, (ii) supercapacitors, (iii) conversion of CO_2 to useful molecules, and (iv) regeneration of enzymatically-active 1,4-NADH from NAD⁺. To the best of the author's knowledge, iridium-ruthenium oxide coatings prepared through thermal decomposition have not been used in any of the abovementioned applications.

CHAPTER 3

3. Statement of Objectives

Previous parts of the thesis indicated that despite the various advantages that metal oxide coatings offer in several electrochemical applications, these coatings still face challenges in terms of their performance consistency, practical applicability limitations, degradation of the oxide film and complexity associated with their production. This is particularly true in the area of charge storage/delivery. In addition, metal-oxide coatings have not been commonly investigated as electrocatalytic hydrogenation materials.

Consequently, the general objectives of this research were to develop bimetallic Ir/Ruoxide coatings on a titanium metal substrate through thermal decomposition and to investigate their surface, topographical, morphological, structural, physicochemical and electrochemical properties and possible applications in two major areas: (i) charge delivery/storage, and (ii) electrocatalytic hydrogenation.

The following specific objectives were set:

- i. Investigation of the influence of Ir_x -Ru_{1-x}-oxide coatings composition
 - a. on the electrode's ability for charge delivery for possible applications as neural stimulating electrodes, and
 - b. on the coating's capability for charge storage for possible applications as supercapacitor electrodes.
- ii. Investigation of the applicability of the $Ir_{0.8}$ -Ru_{0.2}-oxide coating as a electrohydrogenation cathode material
 - a. for the electrochemical reduction of CO₂ into useful organic molecules in an aqueous electrolyte, and
 - b. for the electrochemical regeneration of enzymatic cofactor 1,4-NADH.

The following chapters in the thesis will address the specific objectives mentioned above. Namely, Chapter 4 will discuss the surface properties of Ir_x -Ru_{1-x}-oxide coatings. In addition, the investigation of the apparent electrochemically active surface area (AEASA) and the charge capacity (CSC) of the prepared coatings will be discussed. Chapter 5 investigates the use of Ir_x -Ru_{1-x}-oxide coatings as supercapacitance electrodes. Chapter 6 presents results on the investigation of electrochemical reduction of CO₂ in an aqueous electrolyte employing an Ir/Ruoxide electrode. Direct electrocatalytic reduction of coenzyme NAD⁺ to enzymatically-active 1,4-NADH employing the Ir/Ru-oxide electrode will be presented in Chapter 7.

Each of the following four chapters is written in a manuscript-based style. In this way, the connection between the above outlined objectives and the achieved outcomes of the research can be more clearly understood.

CHAPTER 4

Large Charge-Storage-Capacity Iridium/Ruthenium Oxide Coatings as Promising Material for Neural Stimulating Electrodes

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Manuscript submitted to Materials, Chemistry and Physics, MATCHEMPHYS-D-14-02471, accepted in March 2015.

4.1 Preface

The following chapter presents a comprehensive investigation of various electrochemical and topographical/structural/morphological properties of Ir_x -Ru_{1-x}-oxide coatings of different compositions (x = 0, 0.2, 0.4, 0.6, 0.8, 1.0) deposited on Ti metal substrate through thermal decomposition. Discussion will be mainly focused on the surface characterization of the above-mentioned coating and its electrochemical behavior, which comprises surface roughness, apparent electrochemically-active surface area (AEASA), charge storage capacity (CSC) and coating stability.

The division of tasks in the following paper was done according to this scheme:

- I. Nehar Ullah designed experiments, prepared samples, performed the experimental work, analyzed results and wrote the manuscript.
- II. Sasha Omanovic provided guidance, helped in interpretation and discussion of results, and corrected the manuscript.

4.2 Abstract

Electrochemical and topographical/structural/morphological properties of thermally prepared Ir/Ru-oxide coatings of various compositions formed on a Ti substrate were investigated. An apparent electrochemically active surface area (AEASA) and charge storage capacity (CSC) were determined. The freshly-prepared $Ir_{0.6}Ru_{0.4}$ -oxide coating was found to offer the largest AEASA and CSC; however, after exposing all the coatings to prolonged extreme electrochemical cycling in phosphate buffered saline pH 7.4, within a 5 V potential window ("torturing"), the $Ir_{0.8}Ru_{0.2}$ -oxide coating yielded both the largest AEASA (1540 cm²) and CSC (27 mC cm⁻²). Under the same experimental condition, the $Ir_{0.8}Ru_{0.2}$ -oxide coating was found to yield by a 56% higher CSC than the current state-of-the-art neural stimulating electrode, Ir-oxide, making it a good candidate for further optimization and possible application as a neural stimulating electrode.

Key words: Ruthenium; Iridium; Oxide films; Charge Storage Capacity; Neural Stimulating Electrodes

4.3 Introduction

The use of neural prosthetics devices ranges from the brain stimulation to lowering of symptoms of various diseases (e.g. Parkinson's, epilepsy, uncontrolled night urination and chronic pain), to the interfacing of brain with artificial limbs and vision restoration [32, 44, 92, 199]. Artificial manipulation of the neural system is done with an externally induced electrical current to mimic normal sensorimotor functions with the help of an implanted neural electrode, which is used as a bridge between the external electronic control device and the biological system (neurons). Implanted electrodes, known as neural stimulating electrodes, stimulate the human neuronal tissues and modulate their behavior. These neural stimulators allow the transfer of information between an artificial device and the nervous system [32, 44, 68, 80, 87].

Effective and safe neural stimulation can be achieved by the use of biocompatible, corrosion resistive, moldable, miniature, stable and high-charge-injection-capable neural stimulation electrodes [5, 87, 96, 200]. To simulate an action potential in nerve, a certain amount of charge injection is required, which must be reversible because an irreversible charge injection or faradaic reaction (electron transfer between the electrode and redox species from the tissue/physiological fluid) can cause neural damage by the release of unwanted species near the electrodes and tissue interface [5, 47, 49, 68, 87, 96].

There are many challenges related to the development of neural stimulating electrodes such as its size, reaction/response with/of the human tissue, lack of stability and charge injection capability (requirement) [5, 68, 113]. Too large electrode size, improper (low) charge injection, low corrosion stability, unsatisfactory biocompatibility and fast fouling are main problems associated with the practical use neural stimulating electrodes [5, 44, 47, 68].

Several metal-based electrode materials have been developed and tested for neural stimulation; titanium, tantalum, titanium nitride, stainless steel, platinum and Pt alloys, iridium, ruthenium and rhodium [5, 32, 111]. Platinum is the most prominent neural stimulation electrode material used in prosthetic devices due to its relatively high biocompatibility [47, 201]. However, due to its low charge injection, softness and dissolution at lower charge density limit its wide spread use [5, 32, 99-100]. Similarly, other well-known electrode materials like silver-silver

chloride and stainless steel also dissolve when come in contact with the biological tissues thus, causing inflammation [96, 111]. Other nobel metals such as pure ruthenium and rhodium have also been investigated as neural electrodes, but these electrodes have certain problems such as low biocompatibility and high cost [40-43]. In order to reduce the cost of neural electrode some cheap transition metals such as nickel, manganese, cobalt and their composites have also been utilized, but these electrodes are also not adequately biocompatible and corrosion resistive [40, 113-114]. In addition to the above mentioned materials, titanium is one of most frequently used implantable metals, because of its non toxic nature and large thermal/electrical resistance. However, its low charge injection and UV photo-activity make it unsuitable for neural stimulation [41, 43, 76, 96, 112]. Pure iridium oxide (IrOx) is a popular material for use in neural stimulating electrodes due to its excellent properties such as high reversible charge storage capacity due to the reversible faradaic reaction ($Ir^{3+} \leftrightarrow Ir^{4+}$) occurring in the oxide phase, and have so-far been considered as the state-of-the-art neural stimulating electrode [32-33, 44, 47, 115]. However, iridium is brittle which makes it difficult to develop flexible micro neural electrodes. Also charge injection performance of IrOx electrodes degrade rather rapidly with time due to their unsatisfactory corrosion stability [44-49]. In order to address this, iridium was investigated by alloying with other metals (platinum, titanium, tantalum or tin) to produce mixed metal oxide electrodes [5, 11, 31, 47, 49, 99, 111, 118-119, 202] and with novel hybrid materials (PEDOT, PPy, liquid crystal polymer) to form mixed Ir/polymer-oxide materials [120-121, 203]. However, degradation of the mixed iridium composite at high current pulsing, loss of performance with cycling, brittleness and reproduction in case of polymers mixed material make these electrodes unsuitable for clinical use [5, 99, 121]. Emerging materials like carbon nanotubes, biopolymer (silk), silicon, functionalized polymers material have also been introduced, with a certain success [44, 77, 81-82, 102, 117, 121, 204-208].

In an attempt to develop new stimulating electrode materials that would address some of the above-mentioned problems, we have investigated various physico-chemical properties and surface topography/morphology of bi-metallic iridium/ruthenium-oxide coatings deposited on a Ti substrate, with the aim of obtaining information that could be useful for their possible future use as neural stimulating electrodes. Ruthenium and iridium were selected as components of the bimetal-oxide electrode due to their high charge storage/injection properties, good electrical conductivity and relatively high electrochemical (corrosion) stability [7-9, 43, 52, 72, 122-126].

It will be shown that the developed electrodes offer a larger apparent electrochemically-active surface area (AEASA) with high charge storage capacity (up to 27 mC cm⁻²) as compared to state-of-the –art neural stimulation electrodes, IrOx and very high corrosion stability even after a prolong exposure to rather extreme potential-cycling conditions. This can potentially enable a higher degree of miniaturization of neural stimulating electrodes and an increase in charge injection capability, thus making the Ir/Ru-oxide electrodes potentially more biocompatible and functional.

4.4 Experimental

4.4.1 Chemicals and reagents

Electrochemical properties, namely *apparent electrochemically-active surface area* (AEASA) and *charge storage capacity* (CSC) of bimetallic Ir/Ru-oxide coatings formed on a titanium substrate were studied in 0.5 M H₂SO₄ (purity 98%, Fisher Scientific 351293) and 0.16 M NaCl phosphate buffered solution (PBS) (pH = 7.4), respectively. The buffer solution was prepared by mixing appropriate amounts of sodium chloride (purity \geq 99.5%, Fluka Chemika 71381), sodium phosphate dibasic (purity 99.5%, Fisher Scientific S374) and sodium dihydrogen phosphate anhydrous (purity 99%, Fluka Chemika 71496). To adjust the pH of the buffer solution, a 5 M NaOH solution (Fisher Scientific SS256) was used. All chemicals were used without further purification. Aqueous solutions were prepared using deionized water of resistivity 18.2 MΩ cm.

4.4.2 Electrode preparation

Ir_xRu_{1-x}-oxide coatings (x = 0, 0.2, 0.4, 0.6, 0.8, 1.0; x is the molar ratio and it refers to the content of pure Ir and Ru metals in the precursor solution) were formed on a flat titanium substrate surface employing a thermal decomposition method. First, 0.15 M coating precursor solution was prepared by dissolving proper amounts of IrCl₃×3H₂O (Acros Organics 195500050) and RuCl₃×xH₂O (Sigma Aldrich 206229) in *iso*-propanol (purity 99.9%, Fisher Scientific A416-1). A titanium plate (purity 99.2% metals basis, Alfa Aesar 10398) of dimensions of 2.54 cm × 2.54 cm with a thickness of 0.2 cm was used as a substrate for the Ir/Ru-oxide coating. The titanium substrate plate was first wet-polished using 600-grit SiC sandpaper [112]. Then, the polished plate was rinsed thoroughly with abundant deionized water and sonicated for 30 minutes in water to remove polishing residue. Next, the polished plate was etched in a boiling solution of hydrochloric acid (33wt. %, Fisher Scientific) and deionized water (1:1 by volume) for 30 minutes [53, 209]. After etching, the plate was again thoroughly rinsed with deionized water and then dried in argon.

The already prepared Ir_xRu_{1-x} precursor coating solution was applied uniformly on the freshly prepared titanium substrate, with a paint brush. After applying a first coat, the sample was placed in an oven at 383 K for 5 minutes in order to vaporize the solvent, followed by annealing of the sample at 773 K in a furnace for 15 minutes. The sample was then removed from the furnace, allowed to cool for 5 minutes, and a second coat was subsequently applied. The same procedure was repeated for six times in order to form a six-layered coating on the titanium substrate (the number of coatings and the annealing process had been previously optimized to yield the best coating stability). Finally, the sample was annealed in the furnace for a period of one hour in order to oxidize the coating to yield Ir_xRu_{1-x} -oxides [11, 19, 118, 194].

4.4.3 Electrochemical measurements

Electrochemical experiments were performed in a three-electrode, two compartment batch electrochemical cell at 295±2 K and atmospheric pressure. A graphite rod was used as the counter electrode (CE) and mercury/mercurous sulphate electrode (MSE; +0.642 V *vs.* SHE) was used as a reference electrode (RE). All the potentials in this paper are expressed with respect to MSE. A graphite rod was, prior to each use, sonicated for 30 minutes in ethanol, followed by a thorough rinsing with water. Ir_xRu_{1-x} -oxide coatings of various compositions, formed on a titanium plate substrate, were used as the working electrodes (WE; note that only one side of the titanium plate was coated with the metal–oxide coating). To expose only the coated side of the WE to the electrolyte, a specially-constructed electrolyte. In order to maintain an oxygen-free electrolyte, argon (99.998% pure) was purged through the electrolyte prior electrochemical measurements for 30 minutes and then continued to be purged during the measurements.

Electrochemical measurements were carried out using an Ecochemic Autolab PGSTAT30 Potentiostat/Galvanostat/frequency response analyser. Cyclic voltammetry (CV) experiments were performed in order to determine an AEASA and CSC values of the Ir/Ruoxide coatings. To investigate the coating stability, the coated electrode was cycled within rather extreme potential limits, between -3.0 to 2.5 V, for 500 cycles at a scan rate, sr = 100 mV s⁻¹ in 0.16 M NaCl phosphate buffer (pH = 7.4); further in the text, this experiment will be termed as electrode/coating "*torturing*" (Figure 4.10, later in the text).

4.4.4 Surface characterization

To investigate the WE surface morphology/topography and map the distribution of Ir, Ru and Ti on the coating surface, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were, respectively, carried out using a Philips XL-30 field-emission scanning electron microscope (FE-SEM). The crystallinity of the oxide coatings was investigated by X-ray diffraction analysis (XRD) employing a Bruker D8 Discovery X-Ray diffractometer using CuK α radiation. Surface roughness of the oxide coatings was investigated using atomic force microscopy (AFM) by employing a NT-MDT Solver Atomic Force Microscope in a semi contact mode.

4.5 Results and discussions

4.5.1 Surface morphology/topography and XRD analysis

In order to investigate surface morphology/topography of the produced coatings, SEM images were taken before and after electrode torturing. Figure 4.1 is a representative example of the results obtained for the $Ir_{0.8}$ -Ru_{0.2}-oxide coating (similar surface morphologies were obtained with other coatings).



Figure 4.1: SEM images of the $Ir_{0.8}$ -Ru_{0.2}-oxide coating (a, b) before and (c, d) after torturing. Images (a, c) present the top-view of the coating surface, while (b, d) represent cross-sectional images of the coatings, illustrating their thickness.

The SEM images show that the $Ir_{0.8}$ -Ru_{0.2}-oxide coating surface is characterized by a "cracked-mud" morphology, which is commonly seen for thermally prepared metal-oxide coatings [72]. After the torturing experiment, the morphology of the coating changed slightly, revealing a rougher surface. This is, in fact, a desired outcome of torturing since it indicates that the increased coating roughness could potentially provide better electrode CSC, which will be discussed in detail later in the text.

A cross-sectional analysis of the coating revealed an average coating thickness of ca. 13 μ m, Figure 4.1(b, d), showing that no thinning of the coating occurred as a result of torturing. This indicates high stability of the coating.

In addition to the SEM analysis presented in Figure 4.1, an EDS elemental mapping was also performed to investigate the distribution of Ru, Ir and Ti on the coating's surface, before and after torturing. The corresponding results are shown in Figure 4.2.



Figure 4.2: Elemental mapping analysis of the Ir_{0.8}-Ru_{0.2}-oxide coating performed (a) before and (b) after torturing

The figure shows a uniform distribution of iridium and ruthenium across the substrate surface both before and after torturing. Corresponding chemical composition of the coating was analyzed and relative fractions of the three components, Ir/Ru/Ti, before and after torturing were found to be 0.793/0.133/0.074 and 0.735/0.088/0.178, respectively. Minor localized accumulation of titanium on the coating surface was detected before torturing, as noted in Figure 4.2. However, after torturing, a higher content of titanium and its more uniform distribution on the coating surface was recorded. The only source of titanium is the substrate. Thus, the presence of titanium on the Ir/Ru-oxide coating surface can be attributed to the dissolution of the titanium substrate during the coating preparation procedure. The torturing further increased the titanium content on the coating surface, mostly on the account of decreasing ruthenium content; this is in accordance with literature [125, 210-211], and can be related to the

different reactivity of the three metals towards oxygen. Namely, it has been thermodynamically proven that the affinity of titanium towards oxygen is larger than that of iridium and ruthenium, and titanium, thus, readily diffuses towards the coating surface [212]. Nevertheless, the enrichment of the coating with titanium, as a result of torturing, does not seem to influence the uniform distribution of ruthenium and iridium on the coating surface (Figure 4.2(b)). Similar results were obtained with other coating compositions.

To investigate the crystallographic structure of the $Ir_{0.8}$ -Ru_{0.2}-oxide coating presented in Figure 4.1, XRD analysis of the same coating surface was conducted before and after torturing. Figure 4.3 represents these corresponding XRD results.



Figure 4.3: X-ray diffraction (XRD) patterns of $Ir_{0.8}$ -Ru_{0.2}-oxide coating (a) before and (b) after torturing.

Peaks in the figure show the existence of the tetragonal structure of Ir- and Ru-oxide crystals on the surface [9, 29, 56]. Strong X-ray diffraction peaks of the Ir/Ru-oxide coating films before and after torturing correspond to only the rutile type phase of IrO₂ and RuO₂ crystal structure and no anatase phase was observed. The same applies to titanium oxide, which exists in the rutile phase and as pure titanium [9]. Annealing of the Ir/Ru-oxide coatings at high temperature (773 K) favored the formation of the rutile type phase rather than the anatase type

phase [9, 51]. A comparison of the diffraction peaks in Figure 4.3 before and after torturing reveals the presence of the same phase type distribution within the coating for both precursors' species, Ir and Ru.

The SEM images in Figure 4.1 show that the topography of the $Ir_{0.8}$ -Ru_{0.2}-oxide coating is heterogeneous, i.e. that the surface is rough, especially after the torturing experiment. In order to complement these results and to quantify the surface roughness, we further analyzed the fresh and tortured surfaces employing atomic force microscopy (AFM). The resulting images are, respectively, shown in Figures 4.4(a) and 4.4(b). The figure demonstrates that the Ir_{0.8}-Ru_{0.2}-oxide electrode surface is indeed topographically heterogeneous. The freshly-prepared surface, Figure 4.4(a), displays uniformly distributed smooth hilly-like features, yielding an average surface roughness of 0.221 ±0.055 µm. However, after the torturing experiment, the degree of surface topographical heterogeneity increased both at the micro and sub-micro level, Figure 4.4(b). The corresponding average surface roughness value was determined to be 0.89 ± 0.19 µm. This large (four-fold) increase in surface roughness is a result of continuous cycling of the electrode surface (see Figure 4.10, later in the text) which induces a repetitive oxidation/reduction of Ir- and Ru-oxides. During the oxidation/reduction process, the specific volume of the oxides changes due to the change in content of protons in the crystalline structure, in order to balance the metal charge change. However, the specific volume increase/decrease process is not completely reversible, leading to a gradual increase in surface roughness (Figures 4.4(a) and 4.4(b)); a ca. 300% increase in surface roughness was achieved.



Figure 4.4: Three-dimensional AFM images of the $Ir_{0.8}$ -Ru_{0.2}-oxide coating (a) before and (b) after torturing.

μm

4.5.2 Electrochemical measurements

Electrochemical measurements were performed in order to investigate the electrochemical behaviour of Ir/Ru-oxide coatings in terms of the occurrence of redox reactions in the solid phase (coating) in the potential region of electrochemical water stability and to determine the corresponding charge storage capacity (CSC) of the coatings.

Figure 4.5(a) displays a set of CVs recorded on the freshly-prepared Ir_{0.8}-Ru_{0.2}-oxide electrode in 0.5 M H₂SO₄ in the potential region between hydrogen and oxygen evolution. The shape of the CVs resembles the behaviour typical for the electrochemical response of iridium and ruthenium oxides [22, 51, 72, 213]. Namely, in the anodic scan a very broad peak can be observed at ca 0.1 V, while the cathodic scan outlines two separate peaks, one at ca 0.25 V and the other at more negative potentials, around 0 V, which is rather broad (the peak positions quoted here refer to the CV recorded at the highest scan rate presented in Figure 4.5(a)). These peaks can be deconvoluted into the contributions of Ir(III)/Ir(IV) and Ru(IV)/Ru(III)/Ru(II) redox transitions occurring in the oxide phase [22, 51, 72, 213]. No active-to-passive transitions can be observed, indicating that the coating is corrosion stable under the experimental conditions investigated. Thus, the CVs in Figure 4.5(a) indicate a pseudo-capacitive behaviour of the Ir_{0.8}-Ru_{0.2}-oxide electrode; similarly-shaped CVs were obtained for all the coatings investigated in this work and considering that no additional information can be obtained from those CVs, they are not presented and discussed in the manuscript.

Taking into account the pseudo-capacitive behaviour of the CVs in Figure 4.5 (a), an apparent electrochemically-active surface area (AEASA) of the electrode surface was determined by analyzing the dependence of current at constant potential on the scan rate [72, 214]. It should be noted that the AEASA does not represent the true surface area of the coating exposed to the solution; this is due to the pseudo-capacitive behaviour of the electrode rather than its pure capacitive behaviour. However, it will here be used for the purpose of *relative* comparison of the coatings and the influence of electrode (coating) torturing. Figure 4.5(b) is an example of analysis applied to the Ir_{0.8}-Ru_{0.2}-oxide coating [72, 215-216]. The corresponding current vs. scan dependence shows good linearity (Figure 4.5(b), R²=0.999), with a slope of 11.2 mA cm⁻² V⁻¹ s (or mF cm⁻²), indicating that the Ir_{0.8}-Ru_{0.2}-oxide electrode indeed displays a

capacitive behaviour in the whole potential region studied (note that standard deviation values, displayed by error bars, are small).



Figure 4.5: (a) Cyclic voltammograms of the freshly-prepared $Ir_{0.8}$ -Ru_{0.2}-oxide coating in 0.5 M H₂SO₄ solution recorded at scan rates of (1) 100 (2) 200 (3) 300 (4) 400 and (5) 500 mV s⁻¹. (b) Dependence of the anodic current on the applied scan rate obtained from the voltammograms presented in (a), before torturing the electrode and at a potential of 0.3 V.

Subsequently, an AEASA value of 448 cm² was calculated by dividing the obtained capacitance (slope) by 25 μ F cm⁻¹, the latter being a theoretical electrochemical double layer capacitance [5, 119, 214]. Figure 4.6(hollow bars) shows AEASA values of all the coatings studied in this work, before the torturing experiment. The Ti substrate surface is also presented as a control surface, and as expected, it gave the lowest AEASA value. The graph shows that with an increase in Ir content in the coating, the AEASA value also increases and reaches a maximum for the Ir_{0.6}-Ru_{0.4}-oxide coating.

The SEM (Figure 4.1) and AFM (Figure 4.4) results show that the Ir/Ru-oxide surface roughness increases as a result of electrode torturing. In order to see the effect of torturing on the AEASA, CV measurements presented in Figure 4.5(a) were repeated after the electrode torturing. Figure 4.7 illustrates the corresponding effect; a significant increase in both the anodic

and cathodic current occurred upon torturing, which is in accordance with the conclusions obtained from SEM and AFM experiments. In order to determine a magnitude of AEASA increase, the same analysis presented in the inset to Figure 4.5 was employed; the resulting current vs. scan rate dependence was again linear (not presented, $R^2 = 0.997$) yielding an AEASA value of 1540 cm². Thus, the torturing experiment resulted in a ca. 250% increase in AEASA for this coating. This magnitude of AEASA increase seems to be comparable to that of the surface roughness increase measured by AFM (Figure 4.4).

Figure 4.6(filled bars) presents AEASA values for all the coatings studied in this work. A rather interesting observation is that the new trend in AEASA is different than that obtained before the torturing (hollow bars). A maximum in AEASA was recorded for the $Ir_{0.8}$ -Ru_{0.2}-oxide coating (1540±6 cm²), while the torturing procedure did not produce a significant increase in AEASA for the Ti substrate and the $Ir_{0.6}$ -Ru_{0.4}-oxide coating (note that the latter gave a maximum AEASA before the torturing experiment, Figure 4.6, hollow bars).



Figure 4.6: Apparent electrochemical active surface area (AEASA) of various Ir/Ru-oxide coatings obtained from CVs recorded in $0.5 \text{ M H}_2\text{SO}_4$ before and after electrode torturing. The experimental CV conditions correspond to those in Figure 4.5. The AEASA was determined at a potential of 0.3 V.



Figure 4.7: Cyclic voltammograms of the $Ir_{0.8}$ -Ru_{0.2}-oxide coating in 0.5 M H₂SO₄ recorded at a scan rate, $sr = 100 \text{ mV s}^{-1}$, before and after electrode torturing.

4.5.3 Charge storage capacity (CSC)

Figure 4.6 indicates that the $Ir_{0.8}$ -Ru_{0.2}-, Ru- and Ir-oxide coatings could be good candidates for the development of electrodes for neural stimulation due to their high AEASA and thus potential capability to inject a larger amount of charge per unit geometric surface area (and thus per volume) than the remaining electrodes presented in the figure. Hence, in order to investigate this possibility and to determine whether the charge storage is reversible with respect to the anodic/cathodic cycle (a mandatory requirement for neural stimulating electrodes), a set of CV experiments was performed with both freshly-prepared and tortured Ir/Ru-oxide electrodes, in a 0.16 M saline phosphate buffer at pH 7.4, which is commonly used to simulate physiological body fluids. Figure 4.8 shows a CV of the $Ir_{0.8}$ -Ru_{0.2}-oxide coating recorded after the electrode torturing. The shape reveals the occurrence of Ir(III)/Ir(IV) and Ru(IV)/Ru(III)/Ru(II) redox transitions in the oxide phase, as in Figure 4.5 [22, 51, 72, 213].



Figure 4.8: Cyclic voltammogram of the $Ir_{0.8}$ -Ru_{0.2}-oxide coating recorded in 0.16 M saline phosphate buffer at pH 7.4 at a scan rate, $sr = 20 \text{ mV s}^{-1}$, after electrode torturing.

In order to evaluate the amount of charge that can be delivered during the anodic and cathodic polarization of the electrode, the corresponding areas under the CV curve were integrated, as marked CSC_A and CSC_C on the plot for anodic and cathodic areas. The anodic polarization yielded a CSC_A of 23.3±3.5 mC cm⁻² (this is an average value obtained from CVs recorded at scan rates of 20, 50 and 100 mV s⁻¹), while the cathodic polarization yielded a CSC_C value of 24.3±3.1 mC cm⁻², thus demonstrating that the Ir/Ru redox reactions occurring in the oxide phase are reversible under the experimental conditions investigated. This, in turns, indicates that if a neural stimulating electrode was constructed using the same coating, the corresponding charge storage would also be reversible.

As it can be expected, with a decrease in CV scan rate, the CSC increases; for the $Ir_{0.8}$ -Ru_{0.2}-oxide coating, the CSC (average values for CSC_A and CSC_C) was found to change linearly within the scan rate range used (20 – 100 mVs⁻¹, R²=0.999), yielding an intercept (i.e. maximum CSC) of 27 mC cm⁻². This behavior can be related to the depth-dependent response of the coating [217-218]. Namely, the measured charge depends on both the amount of protons exchanged between the oxide coating and the aqueous solution (related to the occurrence

of Ir(III)/Ir(IV) and Ru(IV)/Ru(III)/Ru(II) redox transitions in the oxide phase) and on the electrochemical double-layer charge. However, assuming the absence of angstrom-size, deep pores in the oxide film, the latter is not scan-rate dependent, within the scan rate range employed. On the other hand, due to the participation of protons in the redox reaction in the oxide phase, the charge associated with the above-mentioned redox reaction is dependent on the availability of protons at the reaction site, and thus on the rate of their diffusion within the oxide phase [218]. Thus, as the scan rate increases, the access of protons to regions deeper beneath the oxide surface becomes more difficult, and the charge measured represents the response of the oxide film closer to the outer film surface. Hence, at some infinitely high scan rate one would measure only the response of the outer oxide film surface. On the other hand, at infinitely small scan rates, one would measure the response of the entire oxide film. Therefore, it could be stated that the abovementioned CSC value (27 mC cm⁻²), obtained at infinitely small scan rate, and represents a maximum CSC value of the Ir_{0.8}-Ru_{0.2}-oxide coating.

Figure 4.9 summarizes the CSC results obtained on all the coatings. The freshly-prepared electrodes exhibit an increasing CSC trend with an increase in Ir content in the coating, reaching a maximum for the Ir_{0.6}-Ru_{0.4}-oxide coating; the trend is the same for both the anodic and cathodic CSC. After torturing, the Ir_{0.8}-Ru_{0.2}-oxide coating yielded a highest CSC value $(27\pm2.32 \text{ mC cm}^{-2})$. A few observations can be made in relation to Figure 4.9; the contribution of both the titanium substrate and titanium oxide incorporated into the Ir/Ru-oxide coating (Figure 4.2) to the CSC can be neglected since the corresponding value is only $0.03\pm0.01 \text{ mC cm}^{-2}$. Further, for all the coatings, the oxide charging/discharging is a reversible process since an average CSC_A/CSC_C ratio is 1.04 ± 0.07 for the fresh and 0.97 ± 0.03 for the tortured coatings. Further, the AEASA/CSC_{average} ratio from Figures 4.6 and 4.9 is similar for both the freshly prepared and tortured coatings, indicating that the increase in AEASA (Figure 4.6) was followed by the increase in their respective charge capacity values (Figure 4.9), despite the fact that the measurements were made in two different electrolytes of different pH values.


Figure 4.9: (a) Anodic charge storage capacity, CSCA and (b) cathodic charge storage capacity, CSCC, of various Ir/Ru-oxide coatings obtained from CVs recorded in 0.16 M saline phosphate buffer at pH 7.4 at a scan rate sr = 20 mV s⁻¹, before and after electrode torturing.

As noted from the previous analysis, the tortured $Ir_{0.8}$ -Ru_{0.2}-oxide coating yielded the highest CSC value among the investigated coatings (27 mC cm⁻² at infinitely small scan rate), which is comparable to values reported in the literature for the state-of-the-art, Ir-oxide [5, 32, 49, 96, 219]. However, Ir-oxide coatings that were reported to offer the highest CSC were found to degrade / deactivate relatively rapidly [44-49]. On the other hand, Ir/Ru-oxide coatings produced in the current work were found to be very stable, even under extreme polarization conditions, i.e. torturing, for example, Figure 4.10 show CVs of the $Ir_{0.8}Ru_{0.2}$ -oxide coating recorded in a wide potential region, between -3.0 V and 2.5 V. At most negative and positive potentials, vigorous evolution of hydrogen and oxygen gas was observed, respectively, while the

middle potential region corresponds to the double layer charging/discharging and to the Ir/Ru-oxide redox transition region. Since corrosion (metal dissolution) is an anodic process, polarization of the electrode to high anodic potentials (in the current work, these are indeed extreme anodic potentials, Figure 4.10) significantly accelerates the metal dissolution. However, the result in Figure 4.10 demonstrates that no dissolution of the Ir/Ru-oxide coating occurred, as evidenced by the overlap of the 100th and 500th polarization cycles (similar results were obtained for other coating compositions studied in the current work, except for the Ru-oxide coating which partially degraded with cyclization). This demonstrates that the produced Ir/Ru-oxide coatings are highly stable and, unlike state-of-the-art Ir-oxide coatings which degraded with cyclization [44-49], can thus represent good candidates for the construction of neural stimulating electrodes. The following should further be noted: the 'torturing' experiment in Figure 4.10 lasted longer than 15h, and the polarization conditions employed were very extreme, i.e. a 5 V potential windows. On the other hand, neural stimulating electrodes apply short current pulses, and they need to be used within the potential window of water stability (<1.23 V), more realistically even in a shorter potential region. Thus, taking this into account, one can conclude that the Ir/Ru-oxide electrodes produced in the current work are, in fact, extremely stable and represent excellent candidates for the use as neural stimulation electrodes. Obviously, their biocompatibility should first be investigated.



Figure 4.10: Cyclic voltammograms of the $Ir_{0.8}Ru_{0.2}$ -oxide electrode recorded in 0.16 M saline phosphate buffer pH = 7.4, at a scan rate, $sr = 100 \text{ mV s}^{-1}$ for 500 cycles. The solid line represents the 100th scan while the dashed line represents the 500th scan.

4.6 Conclusions

Electrochemical and topographical/structural/morphological properties of thermally prepared Ir/Ru-oxide coatings of various compositions formed on a Ti substrate were investigated using various electrochemical and surface characterization techniques. Based on the presented study the following conclusions can be drawn:

The surface of formed Ir/Ru-oxide coatings was characterized by "cracked-mud" morphology, vielding high apparent electrochemically active surface а area (AEASA- up to 1540 cm² for the $Ir_{0.8}Ru_{0.2}$ -oxide coating). EDS elemental mapping confirmed the uniform distribution of Ru and Ir on the coating surface, with a contribution of Ti that originated from the underlying substrate. The Ir/Ru-oxide coatings were found to be of a crystalline structure. Cyclic voltammetry measurements showed that the Ir/Ru-oxide coatings yielded a high charge storage capacity (CSC - up to 27 mC cm⁻² for the $Ir_{0.8}Ru_{0.2}$ -oxide coating), characterized by a reversible charging/discharging cycle. This CSC is by 56% higher than that one offered by the current state-of-the-art neural stimulating electrode, Ir-oxide. AEASA and CSC significantly improved (up to 3 fold), when Ir/Ru-oxide coatings were exposed to prolonged

extreme electrochemical cycling within a 5V potential window ("torturing"). The "torturing" demonstrated that all the Ir/Ru-oxide coatings studied here are very stable, even under extreme polarization conditions. Taking into account the large CSC of the $Ir_{0.8}Ru_{0.2}$ -oxide coating and its high stability, it can be concluded that the material is a good candidate for further optimization for the use as a neural stimulating electrode.

4.7 Acknowledgments

The authors would like to acknowledge the Natural Science and Engineering Research Council of Canada and the University of Engineering and Technology, Peshawar, Pakistan for providing the support for this research.

CHAPTER 5

Iridium-Ruthenium-oxide Coatings for Supercapacitors

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Manuscript submitted to the Canadian Journal of Chemical Engineering, (2014) CJCE-14-0972, accepted in February 2015.

5.1 Preface

The last chapter discussed results on the development of Ir/Ru-oxide coatings as potential candidate materials for applications in the area of neural prosthesis in the form of neural stimulating electrodes. In addition to the topographical/structural/morphological properties of the Ir/Ru-oxide coatings, the electrochemical behavior (AEASA and CSC) was also investigated and the corresponding results were presented. A large CSC and the remarkable stability of the Ir/Ru-oxide coatings along with relatively wide double layer region and redox reversibility, represent the basis for their possible use as supercapacitor electrodes.

Consequently, the current chapter presents and discusses results on the investigation of performance of Ir/Ru-oxide coatings supercapacitor electrode material. The galvanostatic charge/discharge (GCD) measurements of the Ir/Ru-oxide coatings and their stability were investigated and reported in this chapter.

For this paper, the contributions of each author were according to the following:

- I. Nehar Ullah designed experiments, prepared samples, performed the experimental work, analyzed results, and wrote the manuscript.
- II. Mark McArthur provided assistance in analyzing the data and manuscript preparation.
- III. Sasha Omanovic provided guidance, helped in interpretation and discussion of results, and corrected the manuscript.

5.2 Abstract

Electrochemical and topographical/morphological properties of thermally prepared Ir_x -Ru_{1-x}-oxide coatings of various compositions (0 < x ≤ 1) formed on a Ti metal substrate were investigated for their potential application as supercapacitor (SC) electrodes employing scanning electron microscopy and electrochemical techniques of cyclic voltammetry, galvanostatic charge/discharge cycling and electrochemical impedance spectroscopy. Current state-of-the-art, pure ruthenium oxide (RuO₂) coating, showed relatively low performance as compared to other bimetallic Ir_xRu_{1-x} -oxide coatings operated under the same experimental conditions. An electrochemically-activated $Ir_0.4Ru_{0.6}$ -oxide coating yielded the highest capacitance value (85 mF cm⁻²). Prolonged electrochemical cycling of the Ir/Ru-oxide coatings in corrosive phosphate buffered saline pH 7.4 performed within an extreme potential window of 5 V, revealed an excellent stability of the coatings. In addition, this cycling procedure enabled a significant increase in capacitance for all coating compositions. It was shown that the areal capacitance (C_{GA}) of these coatings is strongly dependent upon the nature of the components of which the metal oxide is composed. The addition of IrO₂ to RuO₂ improved the stability and capacitive performance of the thermally prepared Ir/Ru-oxide coatings.

Key words: Iridium/ruthenium-oxide coatings; Pseudocapacitance; Supercapacitor; Stability

5.3 Introduction

The globally increasing population, technological advancement and depletion of traditional energy resources increase the requirements for alternative energy sources. Thus, efforts have been made to develop and implement alternative energy technologies. The popularity of using electrochemistry as one such alternative for novel energy technologies is increasing. One of the most attractive electrochemical methods related to energy storage and delivery comprises of electrochemical capacitors, or supercapacitors (SCs). These electrochemical energy storage devices have gained much attention and are being tested in many potential fields such as energy storage, consumer electronics, fuel cells and emission-free electric vehicles [22, 133, 136].

Supercapacitors utilize conductive electrodes to store energy and deliver charge quickly. Due to their large energy densities, short charging times and longer cycle life than rechargeable batteries, SCs are considered important devices for safe energy storage [51, 135-136]. Several materials have been researched as electrodes for SCs. SCs based on carbon and carbon derivatives, like graphite and glassy carbon, carbon nanotubes (CNTs), activated carbon and carbon fibers (CFs), [132-133, 138, 140-141], conductive polymers [135] and various pure or hybrid metal oxides [4, 51, 136, 143] are worth mentioning. Mixed metal oxides (MMO) for SCs have been extensively investigated due to their possible high energy-storage densities that can enable them to be used as hybrid capacitors (a capacitor that offers battery-like high energy storage density but can be charged/discharged much faster than batteries) [135]. An important advantage that MMOs offer in comparison to traditional electrochemical double-layer capacitors is that the additional charge can be stored/delivered through reversible redox reactions occurring in the solid phase close to the electrode surface [51]. However, the loss of catalytic activity, detachment of the oxide film, limited operating conditions, low capacitance and conductivity, lack of reversibility, low temperature and electrolytic media resistance [34, 135, 144-146] are some of the disadvantages of these MMO pseudocapacitive materials. Much work has been done to mediate these disadvantages. Proper selection of the conductive metal oxide and altering its surface chemistry is key to developing the best SC electrodes.

Ruthenium oxide (RuO₂) has been considered amongst the most efficient and promising materials for SCs due to its high conductivity, relatively high specific capacitance, wide double

layer region and redox reversibility [21-25]. RuO₂ itself has some drawbacks; for example, oxide delamination due to erosion of the surface in acidic media [4, 34-36]. New methods have been developed in order to improve the performance and stability of ruthenium oxide, such as introducing composites of ruthenium with other precursors to form MMOs. Examples of these composites include RuO₂/SnO₂ [148], RuO₂/NiO, RuO₂/Ta₂O₅, RuO₂/Pt [149], RuO₂/IrO₂ [51], RuO₂/CoO, RuO₂/VO_x, RuO₂/TiO₂, RuO₂/MoO₃, RuO₂/CaO and RuO₂/V₂O₄ [4]. A promising hybrid metal oxide can be achieved by combining ruthenium with iridium in a bimetallic Ir/Ruoxide electrode. Iridium is a promising electrode material with relatively high electrochemical (corrosion) stability in acidic medium [9, 123, 153]. Iridium-ruthenium-based metal oxide coatings are good electrode material which are extensively used as anodes or cathodes in many applications, such as in SCs [22, 51], oxygen [29, 52-55], hydrogen evolution electrodes [37-38] and CO₂ reduction electrodes [8, 74], waste water treatment [1, 56-58], chloro-alkali industry [9, 56-57] and clinical applications like neural prosthesis electrodes [70]. To improve Ir/Ru-oxide coatings in the above applications, various methods have been adopted to prepare these coatings [20, 22-23, 38, 43, 51-52, 55, 62-64]. For application in SCs, Hu et al. [22, 51] have developed a hybrid bimetallic Ir/Ru-oxide material by applying a one-step cyclic voltammetric deposition (CVD) method. CV deposition was done successfully to obtain high specific capacitance from bimetallic Ir_xRu_{1-x}-oxide coatings with good chemical stability; however, these bimetallic electrodes showed an undesirable decrease in specific capacitance (C_{sp}) after galvanostatic charge/discharge (GCD) cycling and CV cycling [22, 51]. Consequently, this makes the use of CVD questionable for the purpose of preparing bimetallic Ir_xRu_{1-x}-oxide coatings with nearconstant capacitance.

In an attempt to develop new electrode material that would address some of the abovementioned problems associated with pure RuO_2 and Ir/Ru-oxide composites, we have investigated various physico-chemical properties and surface morphology of *thermally prepared* iridium/ruthenium-oxide coatings of various composition, deposited on a titanium substrate, with the aim of obtaining information that could be useful for their possible future use as SC electrode material. Ruthenium and iridium were selected as components for the bimetal-oxide electrode because their thermally-formed oxides are promising due to their good electrical conductivity and relatively high electrochemical (corrosion) stability [7, 9, 43, 52, 72, 122]. As it will be shown later in the manuscript, the electrodes offered good areal capacitance values with high stability even after a prolonged exposure to rather extreme potential-cycling conditions.

5.4 Experimental

5.4.1 Chemicals and reagents

Electrochemical properties of bimetallic Ir/Ru-oxide electrodes were studied in 0.5 M H_2SO_4 (purity 98%, Fisher Scientific 351293). Activation of the electrodes was carried out in 0.16 M saline phosphate buffered solution (PBS) (pH = 7.4). The buffer solution was prepared by mixing sodium chloride (purity \geq 99.5%, Fluka Chemika 71381), sodium phosphate dibasic (purity 99.5%, Fisher Scientific S374) and sodium dihydrogen phosphate anhydrous (purity 99%, Fluka Chemika 71496). A 5 M NaOH solution (Fisher Scientific SS256) was used to adjust the pH of the buffer solution. All electrochemical experiments were done at 295 ± 2 K. All chemicals were used without further purification. Aqueous solutions were prepared using deionized water (resistivity 18.2 M Ω cm).

5.4.2 Electrode preparation

Ir_xRu_{1-x}-oxide coatings (x = 0, 0.2, 0.4, 0.6, 0.8, 1.0; x is the molar ratio, and it refers to the content of pure Ir in the precursor solution) were formed on a flat titanium substrate surface employing a thermal decomposition method [70, 74-75, 112]. First 0.15 M coating precursor solution was prepared by dissolving IrCl₃×3H₂O (Acros Organics 195500050) and RuCl₃×xH₂O (Sigma Aldrich 206229) salts in iso-propanol (purity 99.9%, Fisher Scientific A416-1). A titanium plate (1.7 cm ×1.7 cm × 0.2 cm; purity 99.2% metals basis, Alfa Aesar10398) was used as a substrate for the Ir/Ru-oxide coatings. The titanium substrate plate was initially wet-polished using 600-grit SiC sandpaper following the method described in the literature [70, 74-75, 112]. Then, the polished plate was rinsed thoroughly with deionized water and sonicated for 30 minutes in an ultrasonic water bath to remove polishing residue. Next, the polished plate was etched in a boiling solution of hydrochloric acid (33wt. %, Fisher Scientific) and deionized water (1:1 by volume) for 30 minutes [70, 74-75, 209, 220]. After etching, the plate was thoroughly rinsed with deionized water and dried under argon.

The Ir-Ru precursor coating solution was applied uniformly on the freshly prepared titanium substrate with an artist's paint brush. After applying the initial coat, the sample was placed in an oven at 380 K for 5 min in order to vaporize the solvent, followed by annealing of the sample at 773 K in a furnace for 15 min. The sample was then removed from the furnace, allowed to cool in ambient air for 5 min, and a second coat of the precursor solution was applied. The procedure was repeated six times in order to form a layered metal oxide coating on the titanium substrate (the number of coatings and the annealing process had been previously optimized for stability. Finally, the sample was annealed in the furnace in air for a period of one hour in order to further oxidize the coating to yield Ir_xRu_{1-x} -oxides [11, 19, 70, 74-75, 118, 194].

5.4.3 Electrochemical capacitance measurements

Electrochemical experiments were performed in a three-electrode, two compartment cell at 295 ± 2 K and atmospheric pressure. Two graphite rods were used as the counter electrode (CE) and were placed opposite to the working electrode (WE) plate. The CEs were separated from the WE and reference electrode (RE) by glass frits (Ace Glass, Inc., USA) in order to prevent any interference from evolved oxygen and/or hydrogen. The graphite rods were, prior to each use, sonicated respectively for 30 min in ethanol and deionized water. A mercury/mercurous sulphate electrode (MSE; +0.642 V vs. SHE, Radiometer Analytical, XR 200) was used as a reference electrode (RE). Ir_xRu_{1-x} -oxide coatings of various compositionsformed on a titanium plate substrate were used as the working electrodes (note that only one side of the titanium plates were coated with the metal oxide coatings). A speciallyconstructed electrochemical sample holder was used in the electrochemical cell to ensure only a selected 1 cm × 1 cm area of the WE was exposed to the supporting electrolyte. In order to maintain an oxygen-free electrolyte, argon (99.998% pure) was bubbled for 30 min prior to electrochemical measurements and continuously during the measurements.

The electrochemical behavior of Ir/Ru-oxide electrodes was measured using galvanostatic chornopotentiometric charge/discharge (GCD) cycling, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). GCD cycling was used to investigate the areal capacitance (C_{GA}) of the Ir/Ru-oxide electrodes. CV experiments were carried out in order to investigate the electrochemical behaviour of Ir/Ru-oxide coatings in terms of the occurrence

and identification of redox reactions within the GCD potential region. EIS measurements were performed in order to investigate the Ir_xRu_{1-x} -oxide and Ir_xRu_{1-x} -oxide/solution interface impedance. To investigate the coating stability, the coated electrode was cycled within a relatively extreme potential region between the oxygen and hydrogen evolution regions (from -3.0 to 2.5 V vs. MSE) for 500 cycles at a scan rate, *sr*, of 100 mV s⁻¹ in corrosive 0.16 M NaCl phosphate buffer (pH = 7.4); since this procedure revealed that such cycling resulted in a significant increase in electrode capacitance, further in the text, this experiment will be termed as electrode/coating "activation" (Figure 5.2, later in the text).

All electrochemical measurements were performed using a computer-controlled combination potentiostat/galvanostat/frequency response analyzer (Autolab PGSTAT30, Metrohm, NL) controlled by the NOVA software package (v. 1.10; Metrohm, NL). The surface topography of the electrode was analyzed by a Phillips XL-30 field emission scanning electron microscope (FE-SEM).

5.5 Results and discussions

5.5.1 Surface topography/morphology

In order to investigate surface topography/morphology of the produced Ir/Ru-oxide coatings, scanning electron micrographs (SEM) were taken before and after electrode activation. Figure 5.1 is a representative example of the results obtained for the Ir_{0.4}-Ru_{0.6}-oxide coating (A, B) before and (C, D) after activation (similar surface morphologies were obtained with other Ir/Ru-oxide coatings).



Figure 5.1: SEM images of the Ir_{0.4}Ru_{0.6}-oxide coating (A, B) before and (C, D) after activation.

The cracked surface of the thermally prepared metal-oxide coatings can be seen from the figure and is reminiscent of the "cracked-mud" morphology commonly observed for thermally prepared metal-oxide coatings [72, 213]. This is present both before and after activation, which is common for this coating preparation method. Activation decreases the depth of cracks uniformly on the surface while increasing surface roughness (and thus the surface area exposed to the electrolyte), which is desirable since a larger surface area can lead to a larger overall capacitance. In both cases (before and after activation), no degradation of the coatings was visually observed; thus, the coatings remained stable. This argument was strengthened from the analysis of the activation experiments (Figure 5.2).

5.5.2 Coating stability and activation

To activate the Ir/Ru-oxide coatings and investigate their stability, the coated electrodes were cycled within rather extreme potential limits, mentioned earlier. Under these conditions, a poorly attached coating would flake from the surface.



Figure 5.2: Cyclic voltammograms of the $Ir_{0.4}Ru_{0.6}$ -oxide electrode recorded in 0.16 M saline phosphate buffer, pH = 7.4, at a scan rate, sr = 100 mV s-1 for 500 cycles. The 100th (solid curve) and 500th (dashed line) cycles are shown.

Figure 5.2 shows CVs of the Ir_{0.4}Ru_{0.6}-oxide coating before and after activation. As we were expecting for this wide potential range, vigorous evolution of hydrogen gas was observed at the most negative potential (-3.0 V) and oxygen gas evolution was observed at the most positive potential (2.5 V). The intermediate potential region corresponds to the electrochemical double layer region and to the Ir/Ru-oxide redox transition region of the employed Ir_{0.4}Ru_{0.6}-oxide coating. Polarization of the electrode at such high anodic potentials and in the corrosive 0.16 M NaCl solution can pulverize thin metal-oxide coatings from the surface by accelerating metal dissolution [36]. However, Figure 5.2 demonstrates that no dissolution of the Ir/Ru-oxide coating occurred, that is, the 100th and 500th cycles almost overlapped (similar results were obtained for other coating compositions studied in the current work, except for the Ru-oxide coating which degraded with cycling). A modest increase in current after 500 cycles is from the surface

roughening effect, which is beneficial for the application of the material in SCs. Activation lasted longer than 15 h, and the polarization conditions employed were extreme, i.e., a 5 V potential window. Thus, one can conclude that the Ir/Ru-oxide electrodes are stable even under these extreme experimental conditions.

Another important aspect of the continuous cycling experiments was to increase the pseudocapacitive reactions of the coating by restructuring the porous oxides on the surface. In the case of the Ir/Ru-oxides, these pseudocapacitive reactions are from the reversible redox transitions between various oxidation states of the coating's metal constituents, i.e., the $Ru^{2+}/Ru^{3+}/Ru^{4+}$ and Ir^{3+}/Ir^{4+} redox transitions occurring in the oxide phase [22, 51, 72, 213, 221].

Further in the next section we will explain in detail the after effects of the activation by determining the capacitance of the Ir_xRu_{1-x} -oxide coatings. This set of electrochemical experiments will further be termed 'after activation' in the paper.

5.5.3 Capacitive behavior of the coatings

Electrochemical measurements were performed in order to investigate the behaviour of Ir/Ru-oxide coatings in terms of the occurrence of redox reactions in the solid phase (coating) within the GCD potential region and to investigate the corresponding areal capacitance (C_{GA}) of the coatings. Figure 5.3 displays a set of CVs recorded with the Ir_{0.4}-Ru_{0.6}-oxide electrode before (dashed line) and after activation (solid line) in 0.5 M H₂SO₄ within an electrochemical double-layer region. The shape of the CVs shows the typical behaviour of the electrochemical response of iridium and ruthenium oxides [22, 51, 213]. As can be seen from the figure, after activation (solid line), a large increase (6-fold) in current density is observed. This increase in current density is the effect of electrode activation (Figure 5.2), and indicates an increase in areal capacitance of the Ir_{0.4}-Ru_{0.6}-oxide coating. In both the anodic and cathodic scans, wide peaks can be observed at ca. 0.2 V and 0.15 V respectively (the peak positions quoted here refer to the CV recorded after activation presented in Figure 5.3(solid line). These peaks can be related to the Ru²⁺/Ru³⁺/Ru⁴⁺ and Ir³⁺/Ir⁴⁺ redox transitions occurring in the oxide phase [22, 51, 213]. Thus, the CVs in Figure 5.3(solid line) indicate a pseudocapacitive behaviour of the Ir_{0.4}-Ru_{0.6}-oxide electrode. CVs of similar shapes were obtained for all the coatings investigated (data not shown).

To further investigate the capacitive behavior of the Ir/Ru-oxide coating before and after activation, GCD cycling was performed.



Figure 5.3: Cyclic voltammograms of $Ir_{0.4}Ru_{0.6}$ -oxide before (dashed line) and after activating the electrode (solid line) recorded in 0.5 M H₂SO₄ at a scan rates, sr = 100 mV s⁻¹.

GCD cycling of the Ir_xRu_{1-x} -oxide coatings was performed from -0.50 to +0.40 V vs. MSE, corresponding to the potential region in Figure 5.3, in 0.5 M H₂SO₄ solution at 0.1 mA cm⁻². Two sets of electrochemical experiments were done for all Ir_xRu_{1-x} -oxide coatings. The first set of electrochemical experiments was done before activation for all Ir_xRu_{1-x} -oxide coatings to determine the capacitance of the freshly-prepared electrodes. GCD cycling was repeated after coating activation to investigate the effect of activation towards the capacitance values. This repetitive set of electrochemical experiments will further be termed 'after activation' in the paper.

An example of the GCD experiment is shown in Figure 5.4(A) for the $Ir_{0.4}Ru_{0.6}$ -oxide coating before (dashed line) and after activation (solid line), while Figure 5.4(B) summarizes the GCD results obtained for all Ir_xRu_{1-x} -oxide coatings before and after activation. The potential

curve in Figure 5.4(A) represents a charging/discharging response typical for a pseudocapacitive behaviour [22, 140, 221]. Namely, the curves deviate from the classical symmetrical triangular shape expected if the capacitance came uniquely from double-layer charging [222]. Because of the curvature near the top of the charge and bottom of discharge cycle, due to the occurrence of redox reactions in the solid phase (as already mentioned before), the $Ir_{0.4}Ru_{0.6}$ -oxide coating behaves as a pseudocapacitor [221]. The same was observed for the other potential curves for all Ir_xRu_{1-x} -oxide coatings (data not shown).

Figure 5.4(B) compares the areal capacitance (C_{GA} (mF cm⁻²)) of Ir_xRu_{1-x}-oxide coatings before and after activation, calculated using [135]:

$$C_{GA} = \frac{I\Delta t}{\Delta EA}$$
(5.1)

where I (A) is current, Δt (s) is the discharge/charge time, ΔE (V) is the potential window, and A is the geometric area (1 cm²) of the electrode exposed to electrolyte. By examining the areal capacitance values obtained for all Ir_xRu_{1-x}-coatings before activation (hollow symbols), Ir_{0.4}Ru_{0.6}-oxide showed the largest C_{GA} value of $14 \pm 2 \text{ mF cm}^{-2}$. A coating of pure RuO₂ yielded the lowest areal capacitance of $3.0 \pm 0.5 \text{ mF cm}^{-2}$, which was surprising considering that RuO₂ is a proposed next-generation SC electrode material [23, 136, 223-224]. The behaviour of the freshly-prepared (not activated) bimetallic Ir_xRu_{1-x}-oxide coatings in Figure 5.4 (B – open symbols) is strongly affected by the coating composition. With an increase in Ir content, the corresponding capacitance varies and reaches a maximum at x = 0.4, yielding a 'bell-shaped' curve. This indicates that thermally prepared bimetallic Ir/Ru-oxide electrodes possess improved pseudocapacitive properties compared to pure Ru- and Ir-oxide, and strengthens the fact that the addition of iridium to ruthenium considerably enhances the utilization of the bimetallic coating by activating the non-stoichiometric sites of the precursor's species in the coatings [38, 55, 57].



Figure 5.4: (A) Final (500th) full charge/discharge cycle of $Ir_{0.4}Ru_{0.6}$ -oxide before (dashed line) and after activating the electrode (solid line), recorded in 0.5 M H₂SO₄ at current density of 0.1 mA cm⁻². (B) Average areal capacitance (C_{GA}) of various compositions of Ir_xRu_{1-x} -oxide coatings from GCD cycling, before (hollow symbols) and after activation (filled symbols). The data is shown as an average and error bars are included, but are very small and thus not visible.

In order to further investigate the effect of activation, corresponding capacitance values are also presented in Figure 5.4(B) (filled symbols). As can be seen, the activation yielded an increase in capacitance for all compositions, which demonstrates the effectiveness of the activation procedure. Surprisingly, a six-fold increase in capacitance was observed after activation for $Ir_{0.4}Ru_{0.6}$ -oxide coating (from 14 ± 1.5 to 85 ± 2 mF cm⁻²); it is currently unknown why this particular coating composition gave a substantially larger increase in capacitance after activation, in comparison to the other compositions tested. However, in general, the origin of the increase in the areal capacitance after activation can be attributed to an improvement of Ir/Ru redox transitions in the solid phase, namely Ru²⁺/Ru³⁺/Ru⁴⁺ and Ir³⁺/Ir⁴⁺, associated with pseudocapacitance of the Ir_x-Ru_{1-x}-oxide coatings (see Figure 5.3) [22, 51, 72, 213, 221]. During the oxidation/reduction process of electrode activation (Figure 5.2), the specific volume of the oxides changes due to the change in proton number in the bulk structure, occurring as a consequence of the required charge balance to satisfy neutrality. In addition, partially absorption/desorption hydrogen and/or oxygen gas in the bulk of the solid phase close to the outer interface might influence the solid-phase structure, resulting in an increased surface roughness. Thus, the morphology of the oxide surface changes with time, enabling an increased access of protons and easier diffusion into the oxide phase during the charging/discharging process (Figure 5.4(A)) resulting in an increased pseudocapacitance (Figure 5.4(B)). An additional contribution to the capacitance also comes from the increased surface areas area after activation, enabling an increase in the double-layer charge capacitance [24].

The thermal decomposition method for forming Ir/Ru-oxide coatings is seldom reported in the literature. Very few studies have been done with respect to SCs utilizing iridiumruthenium composites. A study by Hu et al. [22, 51] examined hybrid bimetallic Ir/Ru-oxide material developed through a one-step cyclic voltammetric deposition (CVD), and it reported an areal capacitance of 65 mF cm⁻². However, these bimetallic electrodes showed a gradual decrease in capacitance with potential cycling in acidic media. This was not encountered with the electrodes used in the current work, exhibiting an excellent chemical stability, (confirmed by analyzing images in Figure 5.1) and by very good capacitance retention shown in Figure 5.6 later in the text. Pure RuO₂, which was tested in this research work, was also studied by others [25, 213, 225] and an areal capacitance in the range of 35-39 mF cm⁻² was reported in this regard. It was established that the method of preparation is a decisive factor in the performance of the oxide as other studies also reported higher capacitance values for RuO₂ depending on the method of preparation and experimental conditions [4, 24, 150]. Zhu et al. [150], recently developed a carbon quantum dot decorated hybrid RuO₂ electrode that yielded a high specific capacitance value with excellent cycling stability. However, these results cannot be compared to our work because the authors reported specific capacitance values normalized to the active electrode mass, rather than to the electrode surface area. On the other hand, IrO₂, which is the other component of the metal oxide discussed in this paper, was also investigated as SCs material; however due to its high cost, it did not draw too much attention for its potential applications in SCs. [226].

The $Ir_{0.4}Ru_{0.6}$ -oxide coating exhibited the largest areal capacitance (Figure 5.4(B)) of the studied coatings, thus it would be useful to study its behaviour as a function of current density. Figure 5.5 yields important information about the rate capability of the $Ir_{0.4}Ru_{0.6}$ -oxide coating with applied current density during 100 GCD cycles. Numbers above the data in Figure 5.5 indicate the current density at which the measurements were performed.



Figure 5.5: Rate capability plot of an activated $Ir_{0.4}$ -Ru_{0.6}-oxide coating obtained from the GCD cycling in 0.5 M H₂SO₄.Current densities used for GCD measurements are given by the numbers above the data separated by vertical dashed lines.

Figure 5.5 shows a large initial capacitance of ca. 58 mF cm⁻² at 0.1 mA cm⁻² which continuously increases as the surface is further activated, reaching ca. 62 ± 3 mF cm⁻² after the 100th GCD

cycle. It should be noted that this value is lower than that presented in Figure 5.4(B); this is because the activation of the coating in Figure 5.4(B) continued after the 100th GCD cycle, reaching a value of 85 ± 2 mF cm⁻² after the 500th cycle. Increasing the charging/discharging current by a factor of 5, i.e., to 0.5 mA cm⁻², caused the capacitance to decrease to 29.31 ± 0.08 mF cm⁻². The capacitance further decreased to 23 ± 1 mF cm⁻² at 10 mA cm⁻². These drops in capacitance with applied current are typical of metal-oxide-based pseudocapacitive materials [223], and can be attributed to the fundamental oxide film properties of the electrodes. In fact, this behavior can be related to the depth-dependent response of the coating [217-218]. Namely, the measured capacitance depends on both the amount of protons exchanged between the oxide coating and the aqueous solution (related to the occurrence of $Ru^{2+}/Ru^{3+}/Ru^{4+}$ and Ir^{3+}/Ir^{4+} redox transitions in the oxide phase) and on the electrochemical double-layer. However, assuming the absence of angstrom-size, deep pores in the oxide film, the latter is not GCD current dependent, within the current range employed. On the other hand, due to the participation of protons in the redox reaction in the oxide phase, the charge associated with the above-mentioned redox reaction is dependent on the availability of protons at the reaction site, and thus on the rate of their diffusion within the oxide phase [218]. As the current increases, the access of protons to regions deeper beneath the oxide surface becomes more difficult, and thus the capacitance measured represents the response of the oxide film closer to the outer film surface. Hence, at some infinitely high current one would measure only the response of the outer oxide film surface. On the other hand, at infinitely small current, one would measure the response of the entire oxide film.

To understand the MMO's capacitance retention with cycle, the activated $Ir_{0.4}$ -Ru_{0.6}-oxide coating was cycled for 3600 GCD cycles at 0.5 mA cm⁻². Figure 5.6 shows normalized areal capacitance with respect to number of GCD cycles, measured in 0.5 M H₂SO₄. It is interesting to note that the capacitance of $Ir_{0.4}$ -Ru_{0.6}-oxide coating electrode increased even after the electrode had already been activated prior the experiment. This indicates that the metal oxide film undergoes further morphological/structural changes, enabling more of the Ir/Ru redox reactions occurring in the oxide phase. After 3600 GCD cycles, the $Ir_{0.4}$ -Ru_{0.6}-oxide coating has a capacitance retention of 103% (increase) of its initial capacitance value.



Figure 5.6: Variation of normalized capacitance of the activated $Ir_{0.4}$ -Ru_{0.6}-oxide coating recorded in 0.5 M H₂SO₄ with respect to the number of cycles, at the GCD current of 0.5 mA cm⁻², demonstrating the high stability of the material.

The capacitance retention measurements also revealed some information regarding the stability of the Ir/Ru-oxide coating. To further support this, CVs were recorded and compared before and after long-term GCD cycling. Figure 5.7 shows the corresponding CVs of the $Ir_{0.4}$ -Ru_{0.6}-oxide coating measured before (dashed line) and after 3600 GCD cycles (solid line).



Figure 5.7: Cyclic voltammograms of an activated $Ir_{0.4}$ -Ru_{0.6}-oxide coating recorded in 0.5 M H₂SO₄ before (Cycle #500) and after prolonged GCD cycling (Cycle #3600). Scan rate, sr = 100 mV s⁻¹.

The two CV curves are of the same shape, demonstrating that the same redox reactions occurred before and after the prolonged GCD cycling. This evidences that no preferential dissolution of one of the metals in the coating occurred during the prolonged GCD cycling and that the coating composition remained the same. This also indicates high corrosion stability of the coating. A slight increase in current recorded after the prolonged GCD cycling indeed coincides with the result in Figure 5.6 and evidences that the increase in capacitance shown in the latter figure is due to the apparent restructuring of the oxide film to yield a higher surface area (roughness) and/or enable easier diffusion of protons in the oxide phase so a larger (deeper) portion of the oxide film can be utilized.

5.5.4 Electrochemical impedance spectroscopy (EIS)

EIS analysis was used to further understand the capacitive behavior of thermally prepared $Ir_x Ru_{1-x}$ -oxide coatings. Figure 5.8 shows the representative EIS spectra obtained for $Ir_{0.4}$ -Ru_{0.6}-oxide coating measured in 0.5 M H₂SO₄ at 0.4 V vs. MSE (similar EIS responses were obtained for the other Ir/Ru-oxide coatings (data not shown)). To quantify the EIS results, the experimental data (circles) were modeled using non-linear least-squares fit analysis (NLLS) software [227] and the electrical equivalent circuit (EEC) presented in the inset of Figure 5.8. The modeled data are represented by the solid line in Figure 5.8. The model was deemed appropriate as the agreement between the data and the model was excellent. R_s in the EEC represents the solution resistance, R represents the polarization resistance, while CPE is a constant-phase-element, representing the electrode capacitance. The use of constant phase elements instead of pure capacitance is required due to the distribution of relaxation times as a result of the coatings due to large heterogeneous rough structure at the micro scale. An average value of the exponent (n=0.9685 ± 0.0004) of the constant phase element in the data demonstrate that the CPE is indeed capacitive [11, 72, 228].



Figure 5.8: Nyquist plot of the activated $Ir_{0.4}$ -Ru_{0.6}-oxide coating recorded in 0.5 M H₂SO₄ at electrode potential of 0.4 V. The solid line represents the modeled spectra obtained using the equivalent electrical circuit model in presented as the inset to the figure.

After analyzing the spectrum for the Ir_{0.4}-Ru_{0.6}-oxide coating, it is evident that the slope of the spectrum is nearly vertical and steep. This reveals that the Ir_{0.4}-Ru_{0.6}-oxide coating system is entirely capacitive [72], yielding a CPE value of $0.03085 \pm 0.00002 \ \Omega^{-1}s^{n}$. Using the Brug equation [229], the corresponding capacitance was calculated to be 32.4 mF cm⁻². Further, the polarization resistance obtained is R = 2900 ± 100 Ω cm⁻², indicating that the redox reactions occurring in the solid phase at 0.4 V and under steady-state conditions are relatively slow. This is expected for materials that display a predominantly-capacitive behaviour, such as Ir_{0.4}-Ru_{0.6}-oxide coating. Taking the capacitance and resistance values into account, the corresponding time constant of the system was calculated to be RC = 92 s. Thus, both the calculated capacitance and time constant values are in the range of those obtained from GCD measurements presented earlier in the paper (these values would be expected for the GCD current density of ca. 0.3 mA cm⁻², which is in accordance with Figure 5.5). However, it should be noted that the EIS spectra was recorded at constant potential of 0.4 V and with the *ac* amplitude of ±10 mV, thus the reliable comparison to GCD values is not fully possible.

5.6 Conclusions

Electrochemical and morphological properties of thermally prepared Ir/Ru-oxide coatings of various compositions formed on a titanium substrate were investigated for SCs. The surface of thermally formed Ir/Ru-oxide coatings was investigated through scanning electron microscopy (SEM) and was characterized by "cracked-mud" morphology, yielding a stable and rough film coating before and after electrode activation. Galvanostatic charge/discharge (GCD) measurements showed that the Ir/Ru-oxide coatings yielded a high areal capacitance (C_{GA} - up to 85mF cm⁻² for the Ir_{0.4}Ru_{0.6}-oxide coating). State-of-the-art pure RuO₂ coatings showed relatively low performance under the experimental conditions applied. C_{GA} significantly improved when Ir/Ru-oxide coatings were exposed to prolonged electrochemical cycling within a 5 V potential window (activation). The activation also demonstrated that all the Ir/Ru-oxide coatings studied here are very stable, even under extreme polarization conditions, except pure RuO₂ coatings that partially detached from the surface. Thus, the results demonstrate that addition of iridium to ruthenium in bimetallic Ir_xRu_{1-x}-oxide coatings increases stability as well capacitive performance of the bimetallic coatings. Ir_{0.4}Ru_{0.6}-oxide coating exhibit good rate capability and capacitance retention. Electrochemical impedance spectroscopy (EIS) confirmed that the coating is predominantly capacitive by nature.

Taking into account the good C_{GA} value of $Ir_{0.4}Ru_{0.6}$ -oxide coating and its high stability as compared to pure ruthenium or iridium, it can be concluded that the material is a good candidate for further optimization for possible use as a SC electrode.

5.7 Acknowledgements

The authors would like to acknowledge the Natural Science and Engineering Research Council of Canada (NSERC), McGill University and the University of Engineering and Technology, Peshawar, Pakistan for providing the support for this research. MAM would like to acknowledge the funding support of McGill University through the McGill Engineering Doctoral Award (MEDA) program and NSERC.

CHAPTER 6

Electrochemical Reduction of CO₂ in an Aqueous Electrolyte Employing an Iridium/Ruthenium-oxide Electrode

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Manuscript published in the Canadian Journal of Chemical Engineering, 93 (2015) 55-62.

6.1 Preface

The previous two chapters discussed the potential use of Ir/Ru-oxide coatings of different compositions in neural stimulation electrodes and supercapacitance (SCs). However, taking into account high electrical conductivity, good electrochemical (corrosion) stability and the potential for offering an intermediate metal-hydrogen bond strength (Ir-H_{ads} and Ru-H_{ads}), Ir/Ru-oxide coatings could potentially also perform as good electrohydrogenation catalysts. Hence, it was suggested to first investigate the possibility of employing these coatings as cathode material to reduce CO_2 into useful organic molecules, in an aqueous phase under ambient conditions, which is presented in the current chapter 6.

For this paper the contributions of each author were the following:

- I. Nehar Ullah designed experiments, prepared samples, performed the experimental work, analyzed results, and wrote the manuscript.
- II. Irshad Ali provided assistance in manuscript preparation.
- III. Maëlle Jansen assisted in performing the experiments.
- IV. Sasha Omanovic provided guidance, helped in interpretation and discussion of results, and corrected the manuscript.

6.2 Abstract

The electrochemical reduction of CO_2 in an aqueous electrolyte (Briton Robinson buffer, pH=5.82) was investigated using an Ir/Ru-oxide coating deposited on a titanium substrate, as a function of electrode potential and temperature. The results demonstrated that the Ir/Ru-oxide electrode can efficiently be used for the electrochemical conversion of CO_2 into different valuable organic molecules at high faradaic efficiency, 85% and 96% at 295 K and 277 K, respectively. Ethanol was found to be the major electrochemical reduction product remained in the liquid phase, with a minor contribution of methanol, acetone and acetaldehyde. The amount of formed products and the corresponding faradaic efficiency were found to be strongly dependent on electrode potential. A maximum in both was obtained at -1.7 V (vs. MSE). At this potential, lowering the reaction temperature from 295 K to 277 K was found to increase the CO_2 reduction kinetics only at short electrolysis times, while the corresponding faradaic efficiency increased significantly. The presented work demonstrates that the Ir/Ru-oxide electrode can be considered as a good electrode candidate for the electrochemical conversion of CO_2 into usable organic molecules at atmospheric pressure and in aqueous electrolytes.

Key words: Ir/Ru-oxide electrode, Carbon dioxide, Electrochemical reduction, organic molecules, Faradaic efficiency

6.3 Introduction

Carbon dioxide is a major greenhouse gas (largest contributor to the greenhouse effect) with enormous adverse environmental effects [230-234]. Human activities are considered being responsible for excessive CO_2 emission into the ecosystem due to which the amount of CO_2 in the environment is increasing day by day. This high concentration of CO_2 affects the ozone layer and results in an increase in global warming [154, 231, 235-237]. Consequently, many changes on earth take place, such as climate change, temperatures rise and change in weather patterns [233, 238-240]. Therefore, it is extremely important to reduce the level of CO_2 generated and released into the environment in order to minimize the threat of global warming. One way of doing this is by converting CO_2 into useful organic molecules [161, 230, 241-259].

Numerous methods have been used for the conversion of CO₂ into useful products, such as chemical, photochemical, electrochemical and photoelectrochemical [161, 244, 260-266]. Electrochemical reduction of CO₂ is a simple and cost effective method [160, 170, 233, 267-269]. Main advantages of electroreduction of CO₂ are: (i) depending on the country, electrical current could be relatively cheap and thus, the electrons (which are reactants in the CO₂ reduction reaction) could be inexpensive to generate, and (ii) the CO₂ reduction reaction (its mechanism and kinetics) could be controlled conveniently by simply controlling the operation of a power source [8, 270]. However, currently, no commercial process on the electroreduction of CO₂ exists. To bring the technology closer to the commercialization, it is necessary to develop more efficient electrocatalysts (i.e. cathodes), that would offer better selectivity in terms of forming desired product, higher faradaic efficiency.

The main problem related to the reduction of CO_2 is its high (electro) chemical stability. Therefore, the electrochemical CO_2 reduction proceeds only at high cathodic overpotentials, i.e. at potentials significantly more negative than the corresponding equilibrium potential. This large overpotential is due to the initial reduction of CO_2 molecule into the surface-adsorbed $CO_{2,ads}^$ radical (single electron reduction) which is always the first and rate determining step (*rds*) in the CO_2 reduction reaction [230]:

$$CO_2 + e^- \to CO_{2.ads}^- \tag{6.1}$$

Furthermore, in aqueous solutions, the hydrogen evolution reaction (HER) is a side reaction that always occurs in parallel with the CO_2 reduction. The first step in the HER is the formation of adsorbed active hydrogen;

$$\mathrm{H}^{+} + \mathrm{e}^{-} \to \mathrm{H}_{\mathrm{ads}} \tag{6.2}$$

Thus, H^+ can react with the CO_2^- radical adsorbed on the electrode surface (Reaction 6.1), according to the Eley-Rideal mechanism, or H_{ads} adsorbed on the electrode surface can react with the CO_2^- radical adsorbed at the neighbouring electrode surface site, following the Langmuir-Hinshelwood mechanism [271]. The latter reaction is kinetically preferred due to its lower activation energy.

Unfortunately, there is always a competition between CO₂-radical protonation and H₂ production reactions [170, 272-274]:

$$H_{ads} + H^+ + e^- \rightarrow H_2 \tag{6.3}$$

or

$$2H_{ads} \rightarrow H_2 \tag{6.4}$$

Thus, the occurrence of Reactions 6.3 or 6.4 decreases the kinetics and faradaic efficiency of the CO_2 reduction reaction. The negative impact of the HER on CO_2 reduction can be minimized by using organic solvents, but since most organic solvents are not environmentally friendly, their use should be avoided. Another way of minimizing the negative impact of the HER is by designing new electrode materials that would promote Reactions (6.1) and (6.2), but not (6.3) and (6.4).

Various metal electrodes have been used in both aqueous and non-aqueous electrolytes to reduce CO_2 into different organic molecules [275-280]. Main products of CO_2 electroreduction have been found to be methanol, ethanol, acetone and acetaldehyde (in addition to some other products such as CO, oxalic acid and formic acid):

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \tag{6.5}$$

$$2CO_2 + 12H^+ + 12e^- \rightarrow CH_3CH_2OH + 3H_2O$$
(6.6)

$$2\text{CO}_2 + 10\text{H}^+ + 10\text{e}^- \rightarrow \text{CH}_3\text{CHO} + 3\text{H}_2\text{O}$$
(6.7)

$$3CO_2 + 16H^+ + 16e^- \rightarrow CH_3COCH_3 + 5H_2O$$
(6.8)

The preferential occurrence of the above reactions is dependent on the electrocatalytic activity, electrode potential and the composition of the supporting electrolyte [7-8, 230]

The electroreduction of CO_2 employing different electrode systems such as bare metallic electrodes and modified electrodes have been reported in literature [160-161, 230, 281]. The latter electrodes were produced by modifying metal electrode surfaces by nano-particle deposition, doping, alloying and coating [7-8, 282-288]. However, certain problems are associated with these systems such as electrode stability, electrode fouling, low selectivity, low product concentration and low faradaic efficiency [7-8, 289]. In addition, a very large overpotential is needed to reduce CO_2 on some of these electrodes such as Pb, Hg, Tl, Fe, Cr, Mo, Pd, Cd, Ti, Nb, Cu, Sn, Ag, Zn, In and Au.

In an attempt to address some of the above-mentioned drawbacks, we have investigated a possibility of employing a bimetallic iridium/ruthenium-oxide electrode to reduce CO₂ to useful organic molecules, in an aqueous phase at room temperature and atmospheric pressure. The rationale for using a metal-oxide electrode was due to the fact that the CO₂ reduction reaction is a cathodic reaction, and if performed in aqueous solutions containing traces of dissolved heavy metals, cathode deactivation can occur rather rapidly due to the electrochemical deposition of the metals on the cathode surface. However, such a deactivated electrode can easily be're-activated' by anodically dissolving the deposited heavy metals, and due to the very high electrochemical stability of the metal-oxide electrode, the electrode would not dissolve [9, 43, 290-293]. Because of this, the cathode can be re-used over a longer period of time without the need to significantly purify the CO₂-dissolving aqueous electrolyte from heavy metals. Ruthenium and iridium were selected as components of the bimetal-oxide electrode because their thermally-formed oxides are

promising electrocatalysts due to their high electrical conductivity, capability of adsorbing hydrogen reversibly (Reaction 6.4) and electrochemical (corrosion) stability [7-8, 122-125]. In addition, literature revealed that the bimetallic Ru/Ir-oxide composition is more electrochemically stable than pure Ru-oxide and Ir-oxide [9, 43, 52, 72].

6.4 Experimental

6.4.1 Chemicals and reagents

The electrochemical reduction of CO₂ using an Ir_{0.8}Ru_{0.2}.oxide electrode was performed in 0.4 M Briton Robinson buffer at pH 5.82 and temperature 295 K. The buffer was prepared by mixing appropriate amounts of boric acid (purity \geq 99.5%, Sigma Aldrich B7901), acetic acid (purity 99.7%, Fisher Scientific 351271) and phosphoric acid (purity 85%, Fisher Scientific A260) [8]. To adjust the pH of the buffer solution, NaOH solution (5 mol dm⁻³ / certified, Fisher Scientific SS256) was used. All chemical were used without further purification. Aqueous solutions were prepared using deionized water of resistivity 18.2 MΩ cm.

6.4.2 Electrode preparation

An Ir_{0.8}Ru_{0.2}-oxide coating was formed on a flat titanium substrate surface employing a thermal decomposition method. First, a 0.15 M coating precursor solution was prepared by dissolving a proper amount of IrCl₃ × 3H₂O (Acros Organics 195500050) and RuCl₃ × xH₂O (Sigma Aldrich 206229) in iso-propanol (purity 99.9%, Fisher Scientific A416-1). A titanium plate (purity 99.2% metals basis, Alfa Aesar 10398) of dimensions of 2.54 cm × 2.54 cm with a thickness of 0.2 cm was used as a substrate for the Ir-Ru oxide coating. The titanium substrate plate was first wet-polished using 600-grit SiC sandpaper [112]. Then, the polished plate was rinsed thoroughly with abundant deionized water and sonicated for 30 minutes in a water bath to remove polishing residue. Next, the polished plate was etched in a boiling solution of hydrochloric acid (33wt. %, Fisher Scientific) and deionized water (1:1 by volume) for 30 minutes [209, 220]. After etching, the plate was again thoroughly rinsed with deionized water and then dried in argon.

The already prepared Ru-Ir precursor coating solution was applied uniformly on the freshly prepared titanium substrate with a paint brush. After first coating, the sample was placed in an oven at 383 K for 5 minutes in order to vaporize the solvent, followed by annealing of the sample at 773 K in a furnace (type 1300) for 15 minutes. The sample was then removed from the furnace, allowed to cool for 5 minutes, and another coating was applied. The same procedure was repeated for six times in order to form six coatings on the titanium substrate. Finally, the sample was annealed in the furnace for a period of one hour to oxidize the coating [11, 19, 118, 194].

6.4.3 Electrochemical reduction of CO₂

Electrochemical reduction of CO₂ was performed in a three-electrode, two compartment batch electrochemical reactor. Two graphite rods were used as counter electrodes (CE) and were placed opposite to the two sides of working electrode plate, to ensure the uniform electric field. The graphite rods were, prior to each use, sonicated for 30 minutes in ethanol, followed by thoroughly rinsing with water. During measurements, the counter electrodes were separated from the working and reference electrode by a glass frit, in order to prevent the oxygen gas evolved at the CE to get in contact with the WE and get reduced, thus interfering with the CO₂ reduction reaction. A mercury/mercurous sulphate electrode (MSE; +0.642 V vs. SHE) was used as a reference electrode (RE), and all the potentials in this paper are expressed with respect to MSE. An Ir_{0.8}Ru_{0.2}-oxide coating on a titanium plate substrate was used as a working electrode (note that both sides of the plate were coated with the metal-oxide coating). A total geometric area of the WE was 12.5 cm². CO₂ reduction experiments were performed in 0.4 M Briton Robinson buffer solution, at pH 5.82, temperatures of 295 and 277 K and atmospheric pressure. The total electrolyte volume was 80 mL. In order to maintain an oxygen-free electrolyte, argon (99.998% pure) was purged through the electrolyte prior electrochemical measurements, for 45 min. Then, CO₂ (99.99%, MEGS) was bubbled through the electrolyte for 45 min prior electrochemical measurements, and it was continued to be bubbled during the electrochemical measurements to maintain the supporting electrolyte saturated with CO₂.

Electrochemical measurements were carried out using an Ecochemic Autolab PGSTAT30 Potentiostat/Galvanostat. The surface topography of the electrode surface was analyzed by a Phillips XL-30 field emission scanning electron microscope (FE-SEM). The concentration of electrolysis products was determined by gas chromatography. For this purpose, liquid phase samples were taken from the electrochemical cell at a regular time interval via a syringe septum and were analyzed by gas chromatography (HP 5890 gas chromatograph) with a flame ionization detector (FID). All collected samples were injected directly into the gas chromatograph without any pre-treatment. A gas chromatography-mass spectroscopy of the electrolysis product was also conducted using GC-MS *Thermo Scientific* Trace GC Ultra Block Heater SCP Science DigiPREP Jr to narrow down the resulted CO₂ reduction products. ATR spectroscopy was done using a Hyperion microscope and the corresponding ATR objective, connected to a Bruker Tensor 27 FTIR spectroscope.

6.5 Results and discussion

6.5.1 Surface topography



Figure 6.1: SEM micrographs of an Ir-Ru-oxide electrode (A) before and (B) after 8 hours of electrolysis.

Figure 6.1 displays the microstructure of (A) a freshly-prepared Ir/Ru-oxide coating (before electrolysis experiments) and (B) the same coating after 8 hours of electrolysis. The surface is characterized by "cracked-mud" morphology in both cases, which is common for metal-oxide coatings formed by the method used in this work. A cross-sectional analysis of the coating has revealed that an average coating thickness is ca. 13 μ m. XRD analysis (not shown) showed the

existence of crystalline IrO_2 and RuO_2 on the surface. The comparison of the two images reveals that the coating did not change significantly after 8 hours of electrolysis. In fact, the same coating was used in a number of replicate experiments, and as figures presented later in the text show, the corresponding standard deviation was very small. Hence, it could be claimed that the produced Ir/Ru-oxide coating is stable under the conditions employed in experiments presented in this work.

6.5.2 Linear polarization measurements

In order to determine a potential region of CO_2 reduction on an Ir/Ru-oxide electrode, linear polarization measurements were first performed. Figure 6.2(a) shows the response of the Ir/Ru-oxide electrode in the absence (dashed line) and presence (solid line) of CO_2 in the supporting electrolyte.



Figure 6.2: (a) Linear voltammograms recorded in the absence and presence of CO₂ dissolved in a Briton Robinson buffer recorded on an $Ir_{0.8}$ -Ru_{0.2}-oxide electrode. Scan rate, $sr = 20 \text{ mV s}^{-1}$. (b) Cathodic current recorded during the electrolysis of a CO₂ saturated buffer solution at electrode potential of -1.7 V. Temperature, T = 295 K.

Figure 6.2(a) demonstrates that in the absence of CO_2 in supporting electrolyte (dashed line), the cathodic current increases at potentials negative of ca. -1.15 V, which is due to the hydrogen evolution reaction (HER) [160, 273-274]. When the supporting electrolyte was saturated with CO_2 (solid line), the resulting cathodic current increased; this current is a sum of the HER and CO_2 reduction reaction current. However, from the result in Figure 6.2(a), it is not possible to determine the relative proportion of the two currents, but as it will be shown later (Figure 6.6), it appears that the faradaic efficiency for the CO_2 reduction reaction is high at -1.7 V. Thus, the quick electrochemical measurements in Figure 6.2(a) indicated that the reduction of CO_2 on an Ir/Ru-oxide electrode is possible, under the experimental conditions investigated.

6.5.3 Electrolysis measurements

To validate the results obtained from the linear polarization measurements in Figure 6.2(a), electrolysis of a CO₂-saturated solution was performed potentiostatically at various electrode potentials and the concentration of the electrolysis products was analyzed by gas chromatography at selected time intervals. An example of a resulting electrolysis current is presented in Figure 6.2(b). As it can be seen, the electrolysis current remained fairly stable during the entire electrolysis potential. However, a small decrease in current was recorded, indicating minor fouling of the electrode surface by adsorbed reaction products/intermediates (this will be discussed in more detail later in the text – Figure 6.7).



Figure 6.3: Concentration of organic molecules in the liquid phase obtained by reduction of CO_2 using an Ir/Ru-oxide electrode in a batch electrochemical reactor operating at electrode potential of -1.7 V_{MSE} for 8 hours. Temperature, T = 295 K.

Figure 6.3(a) shows the concentration of major products, methanol, ethanol, acetaldehyde and acetone (Reactions 6.5-6.8), formed in the liquid phase at 295 K during the electrochemical reduction of CO_2 at -1.7 V (it should be mentioned that only products remained in the liquid phase at concentrations detectable by gas chromatography are presented). Among the four major products, ethanol was found to be formed at the highest relative yield (percentage). Figure 6.3(a) shows that the concentration of produced ethanol increases gradually as the experiment progresses and finally reaches to 864 mg L⁻¹ after 8 hours. An increase in methanol, acetone and acetaldehyde concentration with time was also recorded, but at a much smaller extent relative to that of ethanol.

Figure 6.3(b) shows the concentration profile of total organic molecules (sum of all individual organic molecules) as a function of time. With an increase in electrolysis time, the concentration of total organic molecules increases and reaches 964 mg L^{-1} after 8 hours
of electrolysis. The trend in Figure 6.3(b) is, basically, governed by that of ethanol (Figure 6.3(a)) as ethanol is the major electrolysis product at all times (ca. 90% of the formed organic molecules).

In summary, the results in Figure 6.3 demonstrate that the electrolysis of CO_2 in an aqueous phase at room temperature and atmospheric pressure using the Ir/Ru-oxide electrode is possible, and that the electrode seems to be selective towards production of ethanol (a liquid-phase product).

6.5.4 Effect of temperature on the electrochemical reduction of CO₂

The above experiments were performed at room temperature (295 K). However, the solubility of CO_2 in an aqueous phase increases with a temperature decrease. Thus, it was interesting to investigate if the electrolysis of CO_2 at a lower temperature would result in an increase in CO_2 reduction rate, and thus an increase in the amount of organic molecules produced.

In order to show the effect of temperature on the concentration of total organic molecules produced as a result of CO_2 electroreduction, experiments were performed under the same conditions as in Figure 6.3 but this time at a lower temperature (277 K). The corresponding results are shown in Figure 6.4, along with the results at 295 K for easy comparison.



Figure 6.4: Concentration of total organic molecules in the liquid phase obtained by reduction of CO_2 using an Ir/Ru-oxide electrode in a batch electrochemical reactor operating at electrode potential of -1.7 V_{MSE} for 8 hours, at two different temperatures.

Figure 6.4 demonstrates that at both temperatures the concentration of organic molecules increases with time. When the CO₂ reduction was performed at 277 K (blue bars), the concentration of produced organic molecules was higher than that at 295 K (red bars). However, with an increase in electrolysis time, the relative differences seems to be decreasing, and at the end of electrolysis time the total organic molecules concentration reached 1027 mg L⁻¹ (vs. 965 mg L⁻¹ at 295 K). Nevertheless, there is no statistically significant difference in organic molecules concentration between the two temperatures at the end of the electrolysis experiment (p = 0.40).

Although the electrochemical reduction of CO_2 is an activation-controlled process, and with an increase in temperature the rate of this process also increases, the results in Figure 6.4 demonstrates opposite. However, knowing that the solubility of CO_2 in aqueous solutions increases with decrease in temperature [160], the initial increase in CO_2 reduction kinetics in Figure 6.4 at 277 K, relative to that at 295 K, is then due to the increase in CO_2 dissolved in the aqueous phase.

6.5.5 Effect of electrode potential on the electrochemical reduction of CO₂

In the previous two experiments, the CO_2 reduction reaction was performed at -1.7 V. The rate of this reaction is dependant not only on temperature, but also on electrode (electrolysis) potential. From the theoretical point of view, with an increase in electrolysis potential to more negative (cathodic) values, one could expect an increase in the electron-transfer kinetics, and thus also an increase in CO_2 reduction kinetics. However, taking into account that the HER is a reaction occurring in parallel with the CO_2 reduction reaction on the Ir/Ru-oxide electrode, and that the former is an electron-transfer limited reaction, as opposed to a mass-transfer limited CO_2 reduction reaction, an increase in electrolysis potential to negative values might result in an increase in the rate of the HER relative to the rate of CO_2 reduction, leading to less organic molecules formed in a given time.

In order verify this, CO_2 reduction experiments were carried out at constant temperature and at different electrode potentials for a period of 8 hours. The corresponding results are plotted in Figure 6.5.



Figure 6.5: Concentration of total organic molecules in the liquid phase obtained by reduction of CO_2 using an Ir/Ru-oxide electrode in a batch electrochemical reactor operating at different electrode potentials and temperatures for 8 hours.

The results demonstrate that by increasing the electrode potential from -1.6 V to -1.7 V. the concentration of total organic molecules produced increased from 550 mg L^{-1} to 965 mg L^{-1} . However, a further increase in the electrode potential from -1.7 V to -1.8 V had a negative impact on the total organic molecules concentration, which decreased to 175 mg L⁻¹ at the highest cathodic potential. Thus, these experiments confirmed that the concentration of total organic molecules produced is strongly dependent on electrode potential. The possible explanation for the observed potential-dependent trend could be related to the slow kinetics of the initial CO_2 reduction reaction step, i.e. the formation of adsorbed CO_{2ads}^{-} radical (Reaction 6.1) at potentials positive of -1.7 V and to the competitive HER. Namely, at low cathodic potentials (-1.60 and -1.65 V) the kinetics of formation of adsorbed $CO_{2,ads}^2$ radical is slow and also the concentration of H_{ads} adsorbed on the electrode surface (Reaction 6.2) is low; consequently, the concentration of total organic molecules produced is low. Increasing the electrode potential from -1.6 V to -1.7 V results in an increase in both the kinetics of adsorbed $\mathrm{CO}^{\text{-}}_{2,ads}$ radical formation and in the surface coverage by H_{ads} adsorbed on the electrode surface, and thus also in an increase in concentration of produced organic molecules. However, a further cathodic increase in electrode potential past -1.7 V seems to promote the HER over CO₂ reduction, and the concentration of produced organic molecules sharply decreases (Figure 6.5). The plot also demonstrates that the same trend is also recorded at a lower electrolysis temperature (277 K).

It should also be mentioned that the four organic molecules (ethanol, methanol, acetaldehyde and acetone) were produced regardless of the electrode potential and temperature.

Although the results presented so far confirm that CO_2 can be electrochemically reduced to valuable products under the experimental conditions applied, one of the main problems of CO_2 electroreduction is the faradaic efficiency, which has been reported in literature to be low in aqueous solutions, predominantly due to the HER [160]. This low faradaic efficiency limits the commercial applicability of the electrochemical CO_2 reduction process. Therefore, the next step in our analysis was to determine the corresponding faradaic efficiency of the CO_2 electroreduction process. Faradaic efficiency values were calculated, for each of the identified products (Reactions 6.5-6.8), employing the following equations [8]:

Efficiency (%) =
$$\frac{Q_{red}}{Q_t}$$
 (6.1)

where

$$Q_{red} = N \times n \times F \tag{6.2}$$

and

$$Q_t = I \times t \tag{6.3}$$

In the above equations Q_t (in coulombs, C) represents the total (measured) charge passed through the electrolysis cell, N (in moles) is the number of moles of organic molecule produced, n is the number of electrons required for the reduction of CO₂ to form a product, F is the Faraday constant (=96485 C mol⁻¹), I (in ampers, A) is the electrolysis current, t (in seconds, s) is the time of electrolysis and Q_{red} (in coulombs, C) is the charge involved in the electroreduction of CO₂ to form a particular product.

The calculated total faradaic efficiencies (for all produced species) are shown in Figure 6.6 as a function of electrode potential, at two different temperatures.



Figure 6.6: Total faradaic efficiency obtained by reduction of CO_2 using an Ir/Ru-oxide electrode in a batch electrochemical reactor operating at different electrode potentials and temperatures for 8 hours.

Figure 6.6 shows that by increasing the electrode potential from -1.6 V to -1.65 V, the faradaic efficiency remains constant (ca. 43%). However, by a further increase in the cathodic potential from -1.65 V to -1.7 V, the faradaic efficiency increased dramatically and reached 85% at 295 K (diamonds) and 96% at 277 K (triangles). A further increase in the cathodic potential from -1.7 V to -1.75 V and then to -1.8 V resulted in a sharp decrease in faradaic efficiency, which is most likely due to the parallel occurrence of the competitive hydrogen evolution reaction (HER), which is dominant at more negative potentials. The origin of the lower faradaic efficiencies at -1.65 V and -1.6 V is could be related to the low surface coverage by $CO_{2,ads}^{2}$ protonation and reduction kinetics, which in turns increases the probability for the H_{ads} to produce H₂. The faradaic efficiency obtained at -1.7 V and 277 K (Figure 6.6) seems to be higher than values reported in the literature for the electrochemical reduction of CO_{2} in aqueous electrolytes on Ru-based electrodes. Thus, a Ru-oxide coating deposited on boron -doped diamond electrode gave a faradic efficiency of 90% [8], while pure Ru-oxide and Ru-oxide doped with Cd and Cu gave efficiencies of 30, 38 and 41%, respectively [7].

6.5.6 Electrode surface fouling

It was mentioned earlier in the text (in relation to Figure 6.2(b)) that the electrolysis current slightly decreased with time, which was prescribed to a possible fouling of the electrode surface by adsorbed organic molecules. To investigate if CO_2 reduction products (or intermediates) indeed adsorbed on the electrode surface, an ATR-FTIR spectroscopy was performed after 8 hours of electrolysis and subsequent abundant rising of the electrode surface by deionized water. The resulting spectrum is shown in Figure 6.7.



Figure 6.7: ATR-FTIR spectrum of CO_2 reduction products adsorbed on an Ir/Ru-oxide electrode surface recorded after 8 hours of electrolysis at -1.7 V.

Several characteristics peaks of different CO_2 reduction products are visible on the spectrum. The corresponding band assignments are listed in Table 6.1.

Table 6.1: Infrared band assignments of CO_2 reduction products adsorbed on an Ir/Ru-oxide surface after 8 hours of electrolysis. The wavenumbers refer to vibrations presented in Figure 6.7.

Wavenumber / cm ⁻¹	Assignment
3080	CH ₃ asymmetric stretching
2990	CH ₃ asymmetric stretching
2887	-C-H alkanes
2823	CH stretches (aldehydes)
2393	OCO asymmetric stretch
2287	-CC- alkynes
1765	C=O stretching of HCO or H ₂ CO
1716	C=O stretch (aliphatic ketones)
1580	CH stretching
1485	CH ₃ asymmetric deformation
1296	C-O stretches
1238	C-O stretches
1135	C-O stretches
940	CH bending

The broad and minor peaks at 3080 cm⁻¹ and 2990 cm⁻¹ are related to the response of the CH₃ asymmetric stretch [294-295]. The small peak at 2887 cm⁻¹ shows the C-H of alkanes while the peak at 2823 corresponds to CH stretch of aldehydes [294]. The medium peak at 2393 cm⁻¹ represent OCO asymmetric stretch and the minor peak at 2287 cm⁻¹ show –CC- of alkynes [294]. The peaks at 1765 cm⁻¹ and 1716 cm⁻¹ represent the C=O stretching of HCO or H₂CO, aliphatic ketones and formaldehyde intermediates, respectively [273, 294]. The two minor peaks at 1580 cm⁻¹ and 1485 cm⁻¹ stand for CH stretching and CH₃ asymmetric deformation, respectively [295]. The three peaks at 1296 cm⁻¹, 1238 cm⁻¹ and 1135 cm⁻¹ are related to the C-O

stretch [273]. Finally, the broad peak at 940 cm⁻¹ represents CH bending [294]. In general, the vibrations visible in the spectrum in Figure 6.7 agree well with those reported in the literature. Thus, FTIR-ATR measurements confirmed that during the electrochemical reduction of CO_2 , some of the formed products/intermediates indeed adsorbed on the Ir/Ru-oxide electrode surface, resulting in a minor fouling of the surface (Figure 6.1(b)). However, by sonicating the electrode surface in acetone for 30 minutes, the adsorbed organic molecule layer can completely be removed and the initial (clean) state of the electrode can fully be re-established (which was confirmed by FTIR-ATR).

6.6 Conclusions

From the results presented in this manuscript, it can be concluded that Ir/Ru-oxide coating can efficiently be used for the electrochemical conversion of CO₂ into different organic molecules at room temperature and atmospheric pressure. Ethanol was found to be the major reduction product, with minor contribution of methanol, acetone and acetaldehyde. The concentration of CO₂ reduction products was found to be dependent on electrode potential. Lowering the reactor temperature from 295 K to 277 K was found to influence only the initial CO₂ reduction kinetics, while at longer electrolysis time (8 hours), no statistical difference in the amount of formed organic molecules was found. The highest concentration of formed products and the highest faradaic efficiency were obtained at electrode potential of -1.7 V. Minor fouling of the Ir/Ru-oxide coating surface was detected after 8 hours of electrolysis, but the electrode surface can easily be cleaned by a short-time sonication in acetone.

6.7 Acknowledgements

The authors would like to acknowledge the Natural Science and Engineering Research Council of Canada, and the University of Engineering and Technology, Peshawar, Pakistan for providing the support for this research.

CHAPTER 7

Direct Electrocatalytic Reduction of Coenzyme NAD⁺ to Enzymatically-active 1,4-NADH Employing an Iridium/Ruthenium-oxide Electrode

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Manuscript published in Material, Chemistry and Physics, 149-150 (2015) 413-417.

7.1 Preface

In Chapter 6, it was confirmed that the $Ir_{0.8}/Ru_{0.2}$ -oxide electrode indeed represents a good cathode material for electrochemical hydrogenation, more specifically, for reduction of CO_2 into usable organic molecules. Based on these findings, further investigation on the applicability of the coating for electrochemical hydrogenation was performed. A very expensive enzyme cofactor, 1,4-NADH, was chosen as a molecule of interest and its electrochemical production (regeneration) from NAD⁺ was investigated. This regeneration reaction requires fast hydrogenation of a produced NAD-radical in order to avoid the production of enzymatically-inactive dimer NAD₂. Hence, the Ir/Ru-oxide coating seemed to be a good candidate material for this purpose.

For this paper the contributions of each author were the following:

- I. Nehar Ullah designed experiments, prepared samples, performed the experimental work, analyzed results, and wrote the manuscript.
- II. Irshad Ali provided assistance in designing the experiments and manuscript preparation.
- III. Sasha Omanovic provided guidance, helped in interpretation and discussion of results, and corrected the manuscript.

7.2 Abstract

A thermally prepared iridium/ruthenium-oxide coating ($Ir_{0.8}Ru_{0.2}$ -oxide) formed on a titanium substrate was investigated as a possible electrode for direct electrochemical regeneration of enzymatically-active 1,4-NADH from its oxidized form NAD⁺, at various electrode potentials, in a batch electrochemical reactor. The coating surface was characterized by 'cracked mud' morphology, yielding a high surface roughness. The NADH regeneration results showed that the percentage of enzymatically-active 1,4-NADH present in the product mixture (i.e. recovery) is strongly dependent on the electrode potential, reaching a maximum (88%) at -1.70 V vs. MSE. The relatively high recovery was explained on the basis of availability of adsorbed 'active' hydrogen (H_{ads}) on the Ir/Ru-oxide surface, i.e. on the basis of electrochemical hydrogenation.

Keywords: Iridium/ruthenium-oxide coatings; Electrochemical reduction; Electron Microscopy; Visible and Ultraviolet Spectrometers; Adsorbed active hydrogen

7.3 Introduction

Nicotinamide adenine dinucleotide, NAD(H), is an enzymatic cofactor of significant industrial and biomedical importance. Nearly 700 enzymes use it as a cofactor in various biochemical processes [185, 296-298]. Furthermore, it is also used in the production of high value-added compounds, e.g. expensive drugs, and for the development of biosensors and bio-fuel cells [299-302]. The main function of NAD(H) in a biochemical process is to shuttle electrons and hydrogen (proton):

$$1,4-\text{NADH}+\text{S}+\text{H}^{+} \xleftarrow{\text{enzyme}} \text{NAD}^{+}+\text{SH}_{2}$$

$$(7.1)$$

However, the major obstacle to its widespread use is the extremely high cost of the reduced form (1,4-NADH). Thus, it is of great importance to develop inexpensive and efficient *in-situ* 1,4-NADH regeneration methods.

Several methods have been investigated in the past to regenerate 1,4-NADH including enzymatic, electrochemical, chemical, photochemical and biological methods [175]. Amongst all these methods, non-enzyme-mediated electrochemical methods have attracted much focus due to their potentially low cost, a simple monitoring of the reaction progress, and no need to add a reducing agent, thus potentially enabling relatively simple product isolation [175, 303-305].

As seen in Figure 7.1, the electrochemical reduction of NAD^+ to enzymatically-active 1,4-NADH (i.e 1,4-NADH regeneration) is a two steps process. Step 2a is considered to be slow due to the slow protonation of the NAD-radical, compared to the dimerization of two neighboring NAD-radicals to produce inactive dimer, NAD_2 (Step 2b) [182, 187-190, 306-310].



Figure 7.1: Reduction of NAD^+ to NAD_2 and enzymatically-active 1,4-NADH.R = adenosine diphosphoribose.

Consequently, the yield (recovery) of enzymatically-active 1,4-NADH regenerated on non-modified electrodes ranges from below 1% on a reticulated vitreous carbon to 76% on Hg [179-184]. However, the authors have previously shown that, if the 1,4-NADH regeneration is performed using a bare (non-modified) glassy carbon and carbon-nano fibers electrodes, a 100% regeneration recovery can be obtained but at high cathodic potentials [306, 311] which is in practice not convenient due to high operating cost related to electricity and low faradaic efficiency.

To address the above-mentioned problems, our laboratory has developed 'surfacemodified' electrodes yielding up to 100% regeneration recovery of 1,4-NADH [187-190]. In this work, we are presenting our results on the regeneration of 1,4-NADH employing an iridium/ruthenium-oxide coating deposited on a titanium substrate. The choice of Ir and Ru was based on the fact that both metals are known to offer an optimum metal-hydrogen bond strength (neither too strong nor too week) [73], thus enabling the formation of 'active' hydrogen at low cathodic potentials and its subsequent use for the (electrochemical) hydrogenation of NADradical (Figure 7.1, step 2a), minimizing the formation of inactive NAD₂ (Figure 7.1, Step 2b)

It will be shown that the employed Ir/Ru-oxide coating is highly electrocatalyticallyactive in producing enzymatically-active 1,4-NADH, enabling an 88% recovery. To the best of authors knowledge, this represents a first report on the use of Ir/Ru-oxide electrodes for the reduction of NAD⁺ and regeneration of 1,4-NADH.

7.4 Materials and methods

7.4.1 Ir/Ru-oxide coating/electrode preparation

 $Ir_{0.8}Ru_{0.2}$ -oxide coating was formed on a flat titanium substrate surface employing a thermal decomposition method. The rationale for using this particular bimetallic composition is related to our previous experiments that demonstrated that this Ir/Ru ratio offers the highest apparent electrochemically active surface area among the investigated Ir/Ru electrodes [70]. For the purpose of producing the $Ir_{0.8}Ru_{0.2}$ -oxide coating, 0.15 M precursor coating solution was prepared by dissolving calculated amounts of $IrCl_3 \times 3H_2O$ (Across Organics 195500050) and $RuCl_3 \times 3H_2O$ (Sigma Aldrich 206229) in *iso*-propanol (purity 99.9%, Fisher Scientific A416-1).

A titanium plate (purity 99.2% metals basis, Alfa Aesar 10398) was used as substrate material. The dimensions of the Ti plate were $25\text{mm} \times 25\text{mm} \times 2\text{mm}$. The titanium substrate was initially wet-polished using 600-grit SiC sandpaper [112] after which it was rinsed thoroughly with abundant deionized water and ultrasonically cleaned for 30 min in a water bath to remove polishing residue. Next, the polished titanium plate was etched in a boiling solution of hydrochloric acid (33wt %. Fisher Scientific) and deionized Water, (1:1 by volume) for 30 min [209, 220]. After etching, the plate was again thoroughly rinsed with deionized water and then dried in argon.

The already prepared Ir/Ru precursor coating solution was applied uniformly on the freshly prepared titanium substrate via paint brushing. After applying the first coat, the sample was placed in an oven at 383 K for 5 min in order to vaporize the solvent, followed by annealing of the sample at 773 K in a furnace for 15 min. The sample was then removed from the furnace, allowed to cool for 5 min, and another coat of precursor solution is applied. The same procedure

was repeated for six times in order to form six-layered coatings on the titanium substrate (the number of coatings and annealing process had already been optimized for best coating stability). Finally, the sample was annealed in the furnace for a period of one hour to oxidize the coating to form $Ir_{0.8}Ru_{0.2}$ -oxides [11, 19, 118, 194].

7.4.2 Electrochemical regeneration of 1,4-NADH

Electrochemical regeneration of enzymatically-active 1,4-NADH from a 1.0 mM NAD⁺ solution in 0.10 M phosphate buffer (pH = 5.80), was performed at 295 K in a three-electrode, two compartment batch electrochemical reactor. NAD⁺ solutions were prepared by dissolving a proper amount of β -NAD⁺ (sodium salt, purity 95%) in phosphate buffer solution. All aqueous solutions were prepared using deionized water (resistivity 18.2 M Ω cm).

The $Ir_{0.8}Ru_{0.2}$ -oxide coated titanium plate substrate was used as a working electrode (WE), wherein both sides of the titanium plate were coated with the $Ir_{0.8}Ru_{0.2}$ -oxidecoating. The total geometric area of the WE was 12.50 cm². Two graphite rods were used as counter electrodes (CE), which were, prior to each use, sonicated for 30 min in ethanol, followed by thorough rinsing with water. During measurements, the CE was separated from the working and reference electrodes by a glass frit, in order to prevent oxygen evolved on it to diffuse to the working electrode and get reduced, thus interfering with the NAD⁺ reduction reaction. A mercury/mercurous sulphate electrode (MSE; +0.642 V vs. SHE) was used as a reference electrolyte, argon (99.998% pure) was purged through the electrolyte prior to, and during electrochemical measurements. The argon purge also ensured convective mass transport of electroactive species to/from the electrode surface. The electrochemical batch reactor was connected to a potentiostat, which was used to apply a constant potential to the working electrode. The progress of the NAD⁺ reduction reaction was monitored by UV and visible spectrophotometry.

To determine the enzymatic activity of the regenerated NADH, activity tests were made according to the regular Sigma Quality Control Test Procedure (EC 1.8.1.4) which was further modified for this purpose using lipoamide dehydrogenase (5.3 U/mg, Calzyme laboratories, Inc. 153A0025) as an enzyme and DL-6,8-thioctic acid amide (Fluka T5875) as a substrate

[187-189, 306]. First, a volume of 0.20 mL of substrate and 0.10 mL of EDTA (Sigma ED4S) were added into 2.60 mL of regenerated 1,4-NADH in a cuvette. The absorbance of the solution at 340 nm was monitored using a UV-Vis spectrophotometer, until reaching a steady state value. Then, 0.10 mL of the enzyme was injected into the cuvette while the absorbance was recorded until reaching a final constant value, signifying that the entire active 1,4-NADH formed during the electrolysis was consumed by the enzymatic reaction.

7.5 Result and discussion

7.5.1 Surface morphology of the Ir_{0.8}Ru_{0.2}-oxide coating

In order to investigate the surface morphology of the produced $Ir_{0.8}Ru_{0.2}$ -oxide coating SEM images were taken before and after 1,4-NADH regeneration experiments. Figure 7.2 shows the surface morphology of (A) a freshly-prepared $Ir_{0.8}Ru_{0.2}$ -oxide coating (before measurements) and (B) the same coating after measurements. A textural structure of the Ir/Ru-metal oxide coating resembles the very typical surface morphology of thermally developed metal oxides, known as a mud-cracked morphology [72, 213]. Surface morphology of the coating is very rough and porous yielding a high corresponding apparent electrochemically active surface area (AEASA) [70], which is of advantage in heterogeneous (electro)catalysis [22, 312]. The XRD analysis (not shown here, but in [70],confirmed the presence of only the rutile type phase of IrO₂ and RuO₂ crystal structure on the coating surface, with the contribution of TiO₂ originated from the underlying Ti substrate.

Figure 7.2 shows that there is no significant change in the surface topography/morphology after using the electrode for NADH regeneration. Therefore, these results show that the developed Ir/Ru-oxide coating is stable under the experimental conditions employed.



Figure 7.2: SEM micrographs of Ir_{0.8}Ru_{0.2}-oxide coating (A) before and (B) after 18 hours of use for NADH regeneration.

7.5.2 Reduction of NAD⁺ on a Ir/Ru-oxide electrode (1,4-NADH regeneration)

Linear voltammetry was conducted using the Ir/Ru-oxide electrode to determine the potential region of NAD^+ reduction. Figure 7.3 shows linear voltammograms of the Ir/Ru-oxide electrode recorded in the absence (dashed line) and presence (solid line) of NAD^+ in the solution.



Figure 7.3: Linear voltammograms of an $Ir_{0.8}Ru_{0.2}$ -oxide coated electrode recorded in 0.10 M phosphate buffer solution in the absence of NAD⁺ (dashed line) and presence (solid line) of 4.0 mM NAD⁺. Scan rate, *sr* = 100 mV s⁻¹.

In Figure 7.3, the response of the Ir/Ru-oxide electrode in the absence of NAD⁺ is as expected. Namely, with an increase in cathodic potential past ca. -1.20 V (dashed line), the resulting current also increases, which is due to the increase in the kinetics of the hydrogen evolution reaction (HER) [187-188, 306]. On the other hand, no NAD⁺ reduction peak was recorded on the Ir/Ru-oxide electrode, but the current in the NAD⁺-containing solution (solid line) was higher than that recorded in the background electrolyte (Figure 7.3), indicating the occurrence of NAD⁺ reduction reaction. The absence of an NAD⁺ reduction peak indicates that the reaction is not mass-transport controlled [313]. In addition, the current recorded in the presence of NAD⁺ in Figure 7.3 (solid line) is the sum of the NAD⁺ reduction and hydrogen evolution reaction (HER) current.

Next, electrolysis experiments were conducted to determine the efficiency of the developed bimetallic $Ir_{0.8}Ru_{0.2}$ -oxide coating in regenerating enzymatically-active 1,4-NADH from NAD⁺. These experiments were performed at various potentials, ranging from -1.30 V to -1.80 V_{MSE} in a batch electrochemical reactor. During electrolysis, samples (aliquots of the electrolyte) were taken from the cell (reactor) at selected time intervals in order to monitor the progress of NAD⁺ reduction reaction by measuring the absorbance at 340 nm. As an example, Figure 7.4 shows time evolution of absorbance at 340 nm, during the reduction of NAD⁺ on the Ir/Ru-oxide electrode at two different electrode potentials. An increase in absorbance with time signifies the gradual accumulation of enzymatically-active 1,4-NADH and/or inactive dimer, NAD₂, in the electrolyte (both products absorb at 340 nm, but reactant NAD⁺ does not). The NAD⁺ conversion rate is faster at -1.70 V, which is due to the larger electron-transfer driving force at more negative potentials.



Figure 7.4: Time dependence of absorbance at 340 nm recorded during electrolysis of 1.0 mM NAD^+ using $Ir_{0.8}Ru_{0.2}$ -oxide coated titanium electrode in a batch electrochemical reactor operated at two electrode potentials.

However, results in Figure 7.4 cannot give any information on the amount of enzymatically-active 1,4-NADH formed in the reactions since both NAD_2 and 1,4-NADH absorb at 340 nm. In order to identify the percentage of enzymatically-active 1,4-NADH in the product mixture, an activity assay was performed using the standard procedure discussed in the experimental section. The assay is based on the following reaction, which requires a stoichiometric quantity of 1,4-NADH:

$$1,4-\text{NADH} + \text{DL-lipoamide} \xrightarrow{\text{lipoamide dehydrogenase}} \text{NAD}^+ + \text{dihydrolipoamide}$$
(7.2)

Hence, one can expect to see a decrease in absorbance at 340 nm during the occurrence of reaction (7.2) due to the oxidation of 1,4-NADH to NAD^+ . Finally, taking into account the initial and final absorbance at 340 nm, the purity of enzymatically-active 1,4-NADH produced (regenerated) by electrolysis was calculated:

Purity (recovery) of 1,4 - NADH(%) =
$$\frac{\left[100 - \left(\frac{A}{A_o}\right) \times 100\right]}{\text{initial NAD}^+ \text{ purity}(\%)} \times 100\%$$
(7.1)

where A stands for final absorbance and A_o is the initial absorbance before Reaction 7.2 starts. The assay was first calibrated using commercially available NADH that contains 98% of enzymatically-active 1,4-NADH.The results obtained employing the Ir/Ru-oxide electrode are shown in Figure 7.5 in which the percentage recovery of enzymatically-active 1,4-NADH is plotted as a function of electrode potential.



Figure 7.5: The percentage recovery of enzymatically active 1,4-NADH produced on an $Ir_{0.8}Ru_{0.2}$ -oxide coated electrode by reduction of 1.0 mM NAD⁺ in a batch electrochemical reactor.

It is evident from Figure 7.5 that the recovery of enzymatically-active 1,4-NADH is strongly dependent on the applied electrode potential. Namely, at a low cathodic potential of -1.30 V the recovery of enzymatically-active 1,4-NADH is only 41%. An increase in the electrode potential from -1.30 V to -1.70 V results in an increase the recovery of enzymatically-active 1,4-NADH to 88%, after which it drops down rather sharply to 32%. This potential-dependent trend could be explained by considering Figure 7.1; it is very clear that the kinetics of

Step 2a is strongly dependent on the concentration of proton. In the case of direct electrochemical reduction of NAD⁺, this hydrogen could be supplied directly from the solvent (water), or as an 'active' hydrogen adsorbed on the Ir/Ru-oxide surface (H_{ads}), which depends on the electrode material used and NAD⁺ reduction potential applied. Considering that both Ir and Ru readily adsorb hydrogen to form a metal-hydrogen bond of an intermediate strength [73] and taking into account our previous works[187-190], it is most likely that Step 2a (Figure 7.1) proceeds through the *electrochemical hydrogenation* of NAD-radical by H_{ads}, rather than by H⁺. Now, referring to Figure 7.5, at low cathodic potential, the concentration of H_{ads} on the electrode surface is low and the kinetics of Step 2a is thus slow, favoring the occurrence of Step 2b; this results in a low recovery percentage of enzymatically-active 1,4-NADH. However, by increasing the cathodic potential towards -1.70 V, the surface concentration (coverage) of H_{ads} also increases, resulting in an increase in the kinetics of Step 2a and thus the relative amount of enzymatically-active 1,4-NADH present in the product mixture. However, a further increase in the cathodic potential to -1.80 V results in a significant decrease in the recovery percentage of enzymatically-ative1,4-NADH (Figure 7.5), which could be explained on the basis of an increased kinetics of competitive hydrogen evolution reaction. Thus, it appears that at potentials negative of -1.70 V, the formation of hydrogen gas (H₂) from H_{ads} is favored [314], rather than Step 2a in Figure 7.1.

7.6 Conclusions

The regeneration of enzymatically-active 1,4-NADH in a batch electrochemical reactor was investigated using an Ir/Ru-oxide electrode. It was determined that the percentage of enzymatically-active 1,4-NADH in the product mixture (recovery) was dependent on the applied electrode potential, showing a 'bell-type' behavior. This trend was explained on the basis of influence of Ir/Ru-oxide surface coverage by adsorbed H_{ads} on the kinetics of NAD-radical protonation, occurring in competition with the hydrogen evolution reaction which also uses H_{ads} . The Ir/Ru-oxide coating (electrode) was found to be stable under the experimental condition employed. The results presented here justify further optimization of the Ir/Ru-oxide coating composition and its morphology and also NADH regeneration experimental conditions, with the goal of further increasing the percentage of 1,4-NADH recovered (possibly at lower cathodic potentials).

7.7 Acknowledgements

The authors would like to acknowledge the Natural Science and Engineering Research Council of Canada and the University of Engineering and Technology, Peshawar, Pakistan for providing the support for this research.

CHAPTER 8

8. Conclusions

This PhD project focused on the development of Ir_x -Ru_{1-x}-oxide coatings on a titanium metal substrate using the thermal decomposition method for possible applications as (*i*) neural stimulation electrodes, (*ii*) supercapacitor electrode material, (*iii*) cathodes for electrochemical reduction of CO₂ to useful organic molecules, and (*iv*) cathodes for direct electrochemical regeneration of enzyme cofactor 1,4-NADH.

Main conclusions from the current research work can be subcategorized into the following sections:

8.1 Electrochemical and topographical/structural/morphological characterization of Ir/Ru-oxide coatings for neural stimulation electrodes

Electrochemical and topographical/structural/morphological properties of Ir_x -Ru_{1-x}-oxide coatings (x = 0, 0.2, 0.4, 0.6, 0.8, 1.0) prepared by thermal decomposition of their inorganic salts on a Ti substrate were investigated using several electrochemical and surface characterization techniques. Based on the current work the following conclusions can be drawn:

- The surface of Ir/Ru-oxide coatings was characterized by the so-called "crackedmud" morphology. EDS elemental mapping confirmed the uniform distribution of the coatings' elements, Ru and Ir, on the metal surface. Atomic force microscopy (AFM) and electrochemical characterization confirmed the high roughness of the coatings.
- ii. The results of XRD analysis demonstrated that the Ir/Ru-oxide coatings are crystalline in nature.
- iii. The apparent electrochemically-active surface area (AEASA) of Ir/Ru-oxide coatings determined from scan-dependent cyclic voltammetry (CV) measurements revealed that the $Ir_{0.8}Ru_{0.2}$ -oxide coating offered the largest AEASA (up to 1540 cm² for a 1cm² geometric surface area).

- iv. The reversible charge storage capacity (CSC) of the Ir/Ru-oxide coatings, measured by CV, showed that the $Ir_{0.8}Ru_{0.2}$ -oxide coating yielded a high charge storage capacity (CSC - up to 27 mC cm⁻²). This CSC is 56% higher than the one offered by the current state-of-the-art neural stimulating electrode, Ir-oxide.
- AEASA and CSC significantly improved (up to 3 fold), when Ir/Ru-oxide coatings were exposed to prolonged extreme electrochemical cycling within a 5 V potential window ("torturing"). The "torturing" experiments also demonstrated that all the Ir/Ru-oxide coatings studied here are very stable, even under extreme polarization conditions.
- vi. Large CSC and AEASA of the Ir/Ru-oxide coatings, accompanied by their good stability, make them good candidate materials for further optimization for the use as neural stimulating electrodes.

8.2 Electrochemical and morphological characterization of Ir/Ru-oxide coatings for supercapacitors (SCs)

Main conclusions of this part of the research work are as follows:

- i. Galvanostatic charge/discharge (GCD) measurements employing the Ir_x -Ru_{1-x}-oxide coatings (x = 0, 0.2, 0.4, 0.6, 0.8, 1.0) were performed. $Ir_{0.4}Ru_{0.6}$ -oxide coating yielded a high areal capacitance (up to 85 mF cm⁻²) while pure state-of-the-art RuO₂ failed to deliver and showed relatively low performance as compared to all mixed bimetallic Ir/Ru-oxide coatings under the experimental conditions applied.
- ii. The C_{GA} values significantly improved (up to six-fold), when Ir/Ru-oxide coatings were exposed to prolonged extreme electrochemical cycling within a 5 V potential window. The prolonged electrochemical cycling also demonstrated that all bimetallic Ir/Ru-oxide coatings are stable, except pure RuO₂ coating which detached under the experimental conditions employed.
- iii. Ir_{0.4}Ru_{0.6}-oxide coating exhibits good rate capability and capacitance retention.
- iv. Electrochemical impedance spectroscopy (EIS) revealed the capacitive nature of the $Ir_{0.4}Ru_{0.6}$ -oxide.

8.3 Electrochemical reduction of CO₂ in an aqueous electrolyte on Ir/Ru-oxide coatings

 $Ir_{0.8}$ -Ru_{0.2}-oxide coating was investigated as a potential cathode material for the electrochemical conversion (reduction) of CO₂ to usable organic molecules at different electrode potentials and temperature. Useful organic molecules (ethanol, methanol, acetaldehyde and acetone) were produced during electrolysis experiments and the corresponding faradaic efficiencies were determined. Main conclusions of this part of the research work are as follows:

- i. $Ir_{0.8}$ -Ru_{0.2}-oxide coating was successfully utilized for the electrochemical conversion of CO₂ into organic molecules in an aqueous electrolyte under ambient conditions (atmospheric pressure and at 277 K and 295 K).
- ii. Ethanol was found to be the major organic component formed by the electroreduction of CO₂.
- iii. The concentration of CO_2 reduction products and the corresponding faradaic efficiency were found to be dependent on electrode potential. The highest concentration of formed products and the highest faradaic efficiency were obtained at electrode potential of -1.7 V.
- iv. Temperature effects were also investigated during these experiments. Lowering the electrolyte temperature from 295 K to 277 K was found to influence only the initial CO_2 reduction kinetics, while at longer electrolysis time (8 hours), no statistical difference in the amount of formed organic molecules was found.
- v. The faradaic efficiency was 85% under ambient conditions at 295 K while 96% at 277 K.

8.4 Direct electrochemical reduction of NAD^+ on Ir/Ru-oxide coatings to regenerate 1,4-NADH

This section of the research work focused on the development of electrodes for the direct electrocatalytic regeneration of enzymatically-active 1,4-NADH from NAD⁺. For this purpose, $Ir_{0.8}$ -Ru_{0.2}-oxide coatings were employed. Main conclusions of the works are listed below:

- i. The regeneration of 1,4-NADH from NAD⁺ in a batch electrochemical reactor employing $Ir_{0.8}$ -Ru_{0.2}-oxide coatings is feasible. The purity (recovery) of 1,4-NADH regenerated on these electrodes is highly potential-dependant showing a 'bell type behaviour'. The origin of this potential dependency can be related to the strength of the metal-hydrogen (M-H_{ads}) bond, and thus to the potential dependence of the H_{ads} electrode surface coverage and H₂ gas production.
- ii. The Ir_{0.8}-Ru_{0.2}-oxide coating (electrode) was found to be stable under the employed experimental condition.
- iii. Considering the low cost of the electrode preparation, the simplicity of the process, and the percentage of recovery (purity) of 1,4-NADH, the $Ir_{0.8}$ -Ru_{0.2}-oxide coating can be considered a good candidate electrode material for regeneration of 1,4-NADH.

In summary, the bimetallic Ir/Ru-oxide coatings investigated in this work displayed larger apparent electrochemically-active surface area (AEASA) and proved to be stable in several novel investigated applications. Addition of iridium to ruthenium enhances the investigated electrode properties in comparison to pure Ir- and Ru-oxide coatings. Thus, Ir/Ru-oxide coatings prepared through thermal decomposition are potentially good candidates for neural stimulation electrodes, supercapacitors and as hydrogenation cathodes in reactions of CO_2 and NAD⁺ reduction to usable molecules.

CHAPTER 9

9. Contribution and Future Work

9.1 Contribution to the knowledge

The following are the major original contributions of this work:

- *i.* Ir/Ru-oxide coatings of various compositions were developed with the aim of improving their apparent electrochemically-active surface area (AEASA) and charge storage capacity (CSC). It was shown that some compositions of iridium-ruthenium oxide coatings (namely, Ir_{0.8}Ru_{0.2}-oxide) yielded a larger AEASA and CSC than pure Ir-oxide (current state-of-the-art neural stimulating electrode) while demonstrating a very high corrosion stability even after a prolonged exposure to extreme potential-cycling conditions. This relatively large AEASA and CSC might help in miniaturization of neural stimulating electrodes and trigger an increase in charge injection capability. Consequently, this might reduce the risks associated with the use of large size neural electrodes. To the best of the author's knowledge, no such similar results in terms of CSC with Ir/Ru-oxide coatings have so far been reported in the literature.
- *ii.* Thermally prepared Ir/Ru-oxide coatings of various compositions were investigated for supercapacitance applications with comparable areal capacitance. Actually, the use of thermal decomposition to produce a bimetal Ir/Ru coating for electrochemical supercapacitance applications represents a novel route which has not been explored previously in literature. The thesis author proved that the produced mixed Ir/Ru-oxide coatings are very stable during extreme potential-cycling conditions. It was proved that the presence of Ir in the Ir/Ru-oxide coating material can significantly enhance the surface properties in terms of stability and charge deliverance.
- *iii.* The author of the thesis also investigated Ir/Ru-oxide coatings for the electrochemical reduction of CO₂. This use of the bimetallic oxide coating as a cathode proved to be successful. Employing Ir/Ru-oxide coatings for the electrochemical reduction of CO₂ was

done for the first time. The process entailed the production of organic molecules of ethanol, methanol, acetaldehyde and acetone at a significant faradaic efficiency. Electroreduction of CO_2 was found to be dependent on the electrode potential.

iv. First use of a Ir/Ru-oxide coating cathode capable of regenerating expensive cofactor, nicotinamide adenine dinucleotide 1,4-NADH from NAD⁺ at a high relative yield.

9.2 Suggestions for future work

The use of Ir/Ru-oxide coating is still in its first stages in above mentioned applications and it is in the author's opinion that further research should be undertaken to get a better understanding of the properties of this coating in an attempt to employ them in different novel applications such as the ones mentioned in the previous section. For this purpose, the author suggests the following:

- *i.* Ir/Ru-oxide coatings were demonstrated to have large AEASA and CSC with higher corrosion stability. As the author already mentioned, this CSC is 56% higher than the current state-of-the-art neural stimulating electrode, Ir-oxide. The biocompatibility of Ir/Ru-oxide coatings still needs to be investigated. *In-vitro* and *in-vivo* experiments are recommended to be performed in order to evaluate the performance of these Ir/Ru-oxide coatings as neural electrodes.
- *ii.* Thermal decomposition has been shown to be a simple method to form an Ir/Ru-oxide coating on a Ti substrate metal. It is recommended to apply other coating deposition techniques such as cyclic voltommetric deposition (CVD) and physical vapor deposition (PVD) in an attempt to elucidate the difference in performance between these methods and thermal decomposition.
- *iii.* Ir/Ru-oxide coatings of various compositions were utilized as supercapacitance material. It would be interesting to see the effect of adding a third component like Mn, Co, Ni in preparing ternary mixed metal oxides (Ir/Ru/Mn-Co-Ni-oxide) in order to examine the influence of the third metal oxide component. Rationale for the use of Mn, Ni and Co is their low cost, their pseudocapacitive properties, and their exceptionally high theoretical capacitance.

- Only $Ir_{0.8}Ru_{0.2}$ -oxide was used for the electrochemical reduction of CO₂. The reason for the iv. selection of this particular composition was based on the highest surface roughness and apparent electrochemically-active surface area (AEASA) in previous application such as development of neural stimulation electrodes. However, it might be the case that the composition that worked best with neural stimulation electrodes is not the optimal composition for CO₂ reduction. Hence, it is in the author's opinion that further research should be done to explore the effect of other Ir_x -Ru_{1-x}-oxide coating compositions (x=0, 0.2, 0.4, 0.6, 1) to ascertain the composition that yields the best performance in CO₂ reduction. Also, further research has to be pursued to better understand the CO₂ reduction reaction mechanism in order to optimize the performance. By understanding the reaction scheme, it would be possible to tailor the process towards producing a given desirable product which entails an improvement in the product selectivity. Also, increasing the faradaic efficiency of a given product is possible through employing the right combination of operating conditions and electrocatalysts. This cannot be done until a sound and fundamental comprehension of the reaction pathway is available. In addition to identifying the pathway, the thesis author would also recommend employing different process conditions such as pH, temperature, pressure and cell configuration.
- v. As was the case with CO_2 reduction, in the current research work only one composition of Ir/Ru-oxide coatings (i.e. $Ir_{0.8}Ru_{0.2}$ -oxide) was chosen for the regeneration of 1,4-NADH from NAD⁺. It would be very advantageous if the regeneration of 1,4-NADH is investigated further through employing other compositions of the Ir/Ru-oxide coatings to get a better

118

understanding of the influence of compositions on the process performance.

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