

**DEVELOPMENT OF HIGH TEMPERATURE  
PROTON EXCHANGE MEMBRANE WATER  
ELECTROLYSER FOR GENERATION OF PURE  
HYDROGEN AND OXYGEN**

**VARAGUNAPANDIYAN N**



**DEPARTMENT OF CHEMICAL ENGINEERING  
INDIAN INSTITUTE OF TECHNOLOGY DELHI  
NEW DELHI - 110016  
MARCH 2015**

© Indian Institute of Technology Delhi (IITD), New Delhi, 2015

**DEVELOPMENT OF HIGH TEMPERATURE  
PROTON EXCHANGE MEMBRANE WATER  
ELECTROLYSER FOR GENERATION OF PURE  
HYDROGEN AND OXYGEN**

by

**VARAGUNAPANDIYAN N**

**Department of Chemical Engineering**

Submitted

in fulfillment of the requirements of the degree of

**Doctor of Philosophy**

to the



**INDIAN INSTITUTE OF TECHNOLOGY DELHI**

**MARCH 2015**

## **CERTIFICATE**

This is to certify that thesis entitled “**Development of high temperature proton exchange membrane water electrolyser for generation of pure hydrogen and oxygen**” submitted by **Mr. Varagunapandiyan N** to the Department of Chemical Engineering, Indian Institute of Technology Delhi, New Delhi, for fulfillment of the requirements for the award of Doctor of Philosophy in Chemical Engineering is a record of bonafide work carried out by him. He has worked under my guidance and supervision and has fulfilled the requirements, which to my knowledge, has reached the requisite standard for the submission of the thesis.

The research report and results presented in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.

**Suddhasatwa Basu**  
**Professor and Head**  
**Department of Chemical Engineering**  
**Indian Institute of Technology Delhi**  
**New Delhi 110016, India**

## ACKNOWLEDGEMENTS

First of all, I would like to express my sincere gratitude and heartiest thanks to my guide and mentor **Prof. Sudhasatwa Basu** for his sincere guidance, keen interest and continuous encouragement. He has always shown immense patience and dedicated interest for rectifying my mistakes and improving my skills through discussions by devoting his invaluable time. I am fortunate enough to work under his supervision. He has influenced me both in academic and personal front.

I wish to thank my committee members, Dr. Anupam Shukla, Prof. A. N. Bhaskarwar and Prof. A. Ramanan, for their valuable suggestion and requisite guidance on technical issues during the research work. Encouragement and constant support from Dr. Anupam Shukla throughout my research work is greatly acknowledged. I am also grateful to all the faculty members for their help and cooperation whenever needed.

I wish to thank Council of Scientific and Industrial Research organization (CSIR) for financial support during the execution of research work. I thank all the non teaching staff of Chemical Engineering Department for their help and support, Centre for Polymer Science and Engineering for providing me SEM and EDX facilities and Department of Physics and Chemistry for TEM and XRD facilities.

It was great pleasure to work in fuel cell laboratory. I am thankful to Dr Debika Basu, Dr. Anand Singh, Dr. Amit Kumar Gupta, Dr. Rajalekhmi Chockalingam, Mr. Pankaj Kumar Tiwari, Dr. Gurpreet Kaur, Mr. Shaneeth M., Mrs Jyoti Goel, Mr. Amandeep Jindal, Mr. Harikrishnan N., Dr. Merajul Islam, Mrs. Neetu Kumari, Ms. Ieeba Khan, Mr. Nimai Bhandary, Ms. Garima, Ms. Anu, Mr. Amol, Ms. Criti Mahajan, Mr. Assem Sharma, Mr. Sarthak Nigam,

Mr. Deepak and all other lab members. I would like to thanks Mr. Sunder Singh for his kind support during entire period.

I wish to express my heartfelt thanks to Mr. Vishesh Kumar for allowing me to use Design Lab and furnaces during my research work. I wish to thank all the laboratory and office staff of Chemical Engineering Department especially Mr. Ashish and Mr. Chandan Singh for their encouragement, help and assistance.

I must express my heartiest thanks to my parents Mr. R. Natarajan and Mrs. Ganambal for their well wishes. I sincerely thank my elder brother Mr. N. Annadurai and his wife Mrs. B. Meenakshi. I should not forget my in-laws Mr. V. Sadhasivam and Mrs. R. Siraivani and brother-in-law Mr. S. Stalin who supported me in these years and help me to take challenges through devotion and hard work.

The research would not have been possible without the support of my wife S. Ezhilarasi. I will always be thankful to her for tremendous patience and encouragement to generate positive thoughts and strength inside me to accomplish the ultimate goal.

**Varagunapandiyam N**

## ABSTRACT

Proton exchange membrane water electrolyser (PEMWE) splits water into oxygen and pure hydrogen by oxygen evolution reaction (OER) at anode and hydrogen evolution reaction (HER) at cathode. Water splitting may be more efficient in high temperature PEMWE because of the higher kinetics of electrocatalyst and conductivity of membrane. Although the work on high temperature PEM fuel cell is reported in literature, the same is not true for high temperature PEMWE. To reduce energy consumption in PEMWE, RuO<sub>2</sub> and RuO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> electrocatalysts are tried as anode electrocatalyst in high temperature PEMWE. The anode electrocatalysts are prepared by sol-gel procedure with different compositions and at different calcination temperatures for oxygen evolution reaction. The catalysts are characterized by physical and electrochemical characterization techniques. Physical characterizations are carried out to study the thermal stability, oxygen-metal bond formation, crystalline phase and size, particle size, surface morphology, elemental analysis and elemental mapping by thermogravimetry analysis (TGA), fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) pattern, transmission electron microscope (TEM), scanning electron microscope (SEM) and energy dispersive X-ray (EDX), respectively. Electrochemical characterization is carried out to study the OER on prepared electrocatalyst by cyclic voltammetry (CV), chronoamperometry (CA) in 1.0 M H<sub>3</sub>PO<sub>4</sub> and 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte. Additionally, the effect of electrolyte temperature (25-90 °C) on oxygen evolution reaction is studied and apparent activation energy is estimated from chronoamperogram. The maximum current density (17.27 mA cm<sup>-2</sup>) at 1.2 V is achieved for 90%RuO<sub>2</sub>-10%Ta<sub>2</sub>O<sub>5</sub> anode electrocatalyst calcined at 500 °C in CV experiment using 1.0 M H<sub>3</sub>PO<sub>4</sub> electrolyte at 90 °C. LSV is carried out to understand the OER electron pathway mechanism using rotating ring disk electrode (RRDE) with different rotations (800 to 2000 rpm). LSV of RuO<sub>2</sub> and 90%RuO<sub>2</sub>-10%Ta<sub>2</sub>O<sub>5</sub> electrocatalyst calcined at 500 °C follows 3.8 and 2.68 electron

pathway mechanism for OER. Since proton exchange membrane, Nafion 117, dry up at high temperature ( $>100\text{ }^{\circ}\text{C}$ ) leading to severe loss in ionic conductivity, phosphoric acid doped polybenzimidazole (PBI) membrane is used as electrolyte in the present work. The measured conductivity of 14 M  $\text{H}_3\text{PO}_4$  acid doped PBI membrane is 0.012 S/cm at  $150\text{ }^{\circ}\text{C}$ .  $\text{RuO}_2$  and  $\text{RuO}_2\text{-Ta}_2\text{O}_5$  electrocatalysts are tested in PEMWE for splitting of water using 14 M  $\text{H}_3\text{PO}_4$  acid doped PBI membrane as proton exchange electrolyte and Pt black as cathode catalyst. Gold plated titanium mesh is used as current collector and gold plated titanium monopolar plate (TMP) is used as an end plate and water vapour delivery system at the anode. PEMWE showed best performance for 90% $\text{RuO}_2$ -10% $\text{Ta}_2\text{O}_5$  electrocatalyst calcined at  $500\text{ }^{\circ}\text{C}$  and operating at  $150\text{ }^{\circ}\text{C}$  with current density of  $1.1\text{ A cm}^{-2}$  at 1.8 V. However,  $\text{RuO}_2$  used as anode electrocatalyst in PEMWE (at  $80\text{ }^{\circ}\text{C}$ ) gave lower current density of  $0.875\text{ A cm}^{-2}$  at 1.8 V and its performance dipped after 2.8 h. The stability of PEMWE is improved by the addition of tantalum oxide to ruthenium oxide as 90% $\text{RuO}_2$ -10% $\text{Ta}_2\text{O}_5$  anode electrocatalyst showed the stable current density of  $1.1\text{ A cm}^{-2}$  at 1.8 V up to 5.3 h. The product analysis are carried out in gas chromatography using molecular sieve 5A and Propak Q column, which confirms the presence of hydrogen and oxygen with purity of 99.68% and 95.5% respectively. The energy efficiency of PEMWE is estimated as 35.31%. Moreover 90% $\text{RuO}_2$ -10% $\text{Ta}_2\text{O}_5$  anode catalyst found to be more stable compared to  $\text{RuO}_2$  in 5 h operation of PEMWE at  $150\text{ }^{\circ}\text{C}$  and, further, PEMWE anolyte, membrane electrode assembly after PEMWE operation are investigated by FTIR and X-ray photoelectron spectroscopies (XPS) to evaluate degradation.

# CONTENTS

	<b>Page No.</b>
<i>Certificate</i>	<b>i</b>
<i>Acknowledgements</i>	<b>ii-iii</b>
<i>Abstract</i>	<b>iv-v</b>
<i>Contents</i>	<b>vi</b>
<i>List of Figures</i>	<b>x</b>
<i>List of Tables</i>	<b>xvii</b>
<i>Nomenclature</i>	<b>xix</b>
<b>Chapter 1 Introduction</b>	<b>1-14</b>
1.1 Background	1
1.2 Principle of proton exchange membrane water electrolyser (PEMWE)	4
1.3 Thermodynamics of water splitting	5
1.4 PEMWE energy efficiency calculation	8
1.5 Thesis organization	10
References	13
<b>Chapter 2 Literature Review</b>	<b>15-40</b>
2.1 Oxygen evolution reaction (OER) catalysts	15
2.1.1 Dimensionally stable electrodes	16
2.1.2 Anode electrocatalysts for OER in PEMWE	17
2.2 Physical and electrochemical characterization techniques	25
2.3 Motivation and objectives of thesis work	26
References	29

<b>Chapter 3</b>	<b>Experimental</b>	<b>41-58</b>
3.1	Materials	41
3.2	Catalyst preparation	43
3.3	Physical characterization techniques	45
3.4	Electrochemical analysis	47
3.5	Membrane conductivity measurement	49
3.6	PEMWE testing	51
3.6.1	Gold coating of titanium mono-polar (TMP) plate and titanium mesh	51
3.6.2	Fabrication of membrane electrode assembly (MEA)	53
3.6.3	PEMWE setup and operation	54
	References	58
<b>Chapter 4</b>	<b>Results and Discussion on Performance of RuO<sub>2</sub> Anode Electrocatalyst for High Temperature PEMWE</b>	<b>59-80</b>
4.1	Physical characterization techniques	59
4.1.1	X-ray diffraction (XRD) pattern of RuO <sub>2</sub>	59
4.1.2	FTIR of RuO <sub>2</sub>	60
4.1.3	TEM of RuO <sub>2</sub>	62
4.1.4	EDX and SEM of RuO <sub>2</sub>	62
4.2	Electrochemical analysis	64
4.2.1	Rotating ring disk electrode (RRDE)	69
4.3	Performance of RuO <sub>2</sub> in PEMWE	72
4.3.1	Low temperature PEMWE	72
4.3.2	High temperature PEMWE	73

4.4	PEMWE stability test	76
	References	79
<b>Chapter 5</b>	<b>Results and Discussion on Performance of Ruthenium oxide-Tantalum Oxide Anode Electrocatalyst for High Temperature PEMWE</b>	<b>81-124</b>
5.1	Physical characterization techniques	82
5.1.1	X-ray diffraction (XRD) pattern of RuO <sub>2</sub> -Ta <sub>2</sub> O <sub>5</sub>	82
5.1.2	FTIR of RuO <sub>2</sub> -Ta <sub>2</sub> O <sub>5</sub>	84
5.1.3	TEM of RuO <sub>2</sub> -Ta <sub>2</sub> O <sub>5</sub>	87
5.1.4	EDX and SEM of RuO <sub>2</sub> -Ta <sub>2</sub> O <sub>5</sub>	88
5.2	Electrochemical Analysis	93
5.2.1	Effect of compositions of RuO <sub>2</sub> -Ta <sub>2</sub> O <sub>5</sub>	93
5.2.2	Effect of calcination and electrolyte temperature on RuO <sub>2</sub> -Ta <sub>2</sub> O <sub>5</sub>	97
5.2.3	Chronoamperometry of RuO <sub>2</sub> -Ta <sub>2</sub> O <sub>5</sub>	101
5.2.4	Rotating ring disk electrode (RRDE)	104
5.3	Performance of RuO <sub>2</sub> -Ta <sub>2</sub> O <sub>5</sub> in PEMWE	109
5.3.1	Effect of different compositions of RuO <sub>2</sub> -Ta <sub>2</sub> O <sub>5</sub> in PEMWE	109
5.3.2	Effect of operating temperature in PEMWE	111
5.4	PEMWE stability test	114
5.5	Degradation analysis	115
5.6	Product analysis and energy efficiency calculation	120
	References	122
<b>Chapter 6</b>	<b>Conclusions and Summary</b>	<b>125-130</b>
6.1	Scope of future work	128

<b>Appendices</b>	<b>131-138</b>
A Synthesis and characterization of RuO <sub>2</sub> and IrO <sub>2</sub> by polyol method	131
B Stability test for 90% RuO <sub>2</sub> -10% Ta <sub>2</sub> O <sub>5</sub> calcined at different temperatures	136
C Synthesis of composite membranes and testing in PEMWE	137
<b>List of Publications</b>	<b>139</b>
<b>About the Author</b>	<b>141</b>