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

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MARCH 2015

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by

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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.

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ACKNOWLEDGEMENTS

First of all, I would like to express my sincere gratitude and heartiest thanks to my guide and mentor **Prof. Suddhasatwa 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.

Varagunapandiyan 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_2 and RuO_2-Ta_2O_5 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_3PO_4 and 0.5 M H_2SO_4 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^{-2}) at 1.2 V is achieved for 90%RuO_2-10%Ta_2O_5 anode electrocatalyst calcined at 500 °C in CV experiment using 1.0 M H_3PO_4 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_2 and 90%RuO_2-10%Ta_2O_5 electrocatalyst calcined at 500 ^{o}C follows 3.8 and 2.68 electron

pathway mechanism for OER. Since proton exchange membrane, Nafion 117, dry up at high temperature (>100 °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 H_3PO_4 acid doped PBI membrane is 0.012 S/cm at 150 °C. RuO_2 and RuO_2-Ta_2O_5 electrocatalysts are tested in PEMWE for splitting of water using 14 M H_3PO_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%RuO_2-10%Ta_2O_5 electrocatalyst calcined at 500 °C and operating at 150 °C with current density of 1.1 A cm^{-2} at 1.8 V. However, RuO_2 used as anode electrocatalyst in PEMWE (at 80 °C) gave lower current density of 0.875 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%RuO_2-10%Ta_2O_5 anode electrocatalyst showed the stable current density of 1.1 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%RuO_2-10%Ta_2O_5 anode catalyst found to be more stable compared to RuO_2 in 5 h operation of PEMWE at 150 °C and, further, PEMWE anolyte, membrane electrode assembly after PEMWE operation are investigated by FTIR and X-ray photoelectron spectroscopies (XPS) to evaluate degradation.

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