# MODIFICATION OF Ni-YSZ BASED ANODE IN SOLID OXIDE FUEL CELL TO IMPROVE PERFORMANCE UNDER REDOX CYCLES

**PANKAJ KUMAR TIWARI**


**DEPARTMENT OF CHEMICAL ENGINEERING**

**INDIAN INSTITUTE OF TECHNOLOGY DELHI**

**NEW DELHI-110016**

**JUNE 2015**

# MODIFICATION OF Ni-YSZ BASED ANODE IN SOLID OXIDE FUEL CELL TO IMPROVE PERFORMANCE UNDER REDOX CYCLES

by

**PANKAJ KUMAR TIWARI**

Department of Chemical Engineering

Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy

to the


**INDIAN INSTITUTE OF TECHNOLOGY DELHI**
**JUNE 2015**

*Dedicated to my parent*

# Certificate

This is to certify that the thesis entitled "**Modification of Ni-YSZ Based Anode in Solid Oxide Fuel Cell to Improve Performance Under Redox Cycles**" being submitted by **Pankaj Kumar Tiwari** to the Department of Chemical Engineering, Indian Institute of Technology, 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

I would like to express my deep and sincere gratitude to my guide and mentor **Prof. Suddhasatwa Basu,** Department of Chemical Engineering, under whose guidance, inspiration, keen interest and support, i had the opportunity to conduct this study. I shall be indebted to him forever for inculcating within me the qualities of confidence, perseverance and a sense of commitment towards one's work. I wish to thank my committee members, Prof. S. Roy, Dr. M. A. Shaikh and Dr. S. Aravindan for their valuable suggestion and requisite guidance on technical issues during the research work. 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. C. Anand Singh, Dr Debika Basu, Dr. Rajalekhmi Chockalingam, Mrs. Jyoti Goel, Mrs. Gurpreet Kaur, Mrs. Nitu, Ms. Ieeba, Dr. Meerajul, Mr. Varagunapandyan N, Mr. Harikishan, Mr. Amandeep Jindal, Mr. Nimay, Mr. Aseem, Mr. Amol, Mr. Deepak, Ms. Garima, Ms. Anu, Ms. Criti and all other lab members. I would like to thanks Mr. Sunder Singh for his kind support during entire period. The support and strength provided by my friends was immense. I would like to thank all of them. When it comes to personal support and strength, i wish to express my heartfelt thanks to my parent. Their unflinching support, patience and love have helped me pursue my dreams.

**Pankaj Kumar Tiwari**

# Abstract

The aim of the present work is to assess the performance of modified Ni-YSZ anodes in SOFC under redox cycles. We have studied the effect of impregnating small amount of transition metal oxides, e.g., $TiO_2$, $CeO_2$ and $Nb_2O_5$ as a support for Ni in Ni-YSZ anode matrix in mitigating rapid degradation of the performance. To inhibit agglomeration in Ni-YSZ anode we have also synthesized $TiO_2$-NiO-YSZ, $CeO_2$-NiO-YSZ, $Nb_2O_5$-NiO-YSZ and single/bi-doped $SrTiO_3$ based anode materials using solid state method and evaluated their performance in electrolyte supported SOFC. Sintering of Ni particles in Ni infiltrated porous YSZ anodes and decrease in triple phase boundary is the reason for performance loss in SOFC. In the present work, the idea of strong metal support interaction (SMSI) has been used to prevent the sintering of Ni particles by introducing $TiO_2$ as support with Ni catalyst. Electrical conductivity variation of porous YSZ matrix impregnated with Ni and $TiO_2$-Ni have been investigated. Single button cells (anode supported) with and without $TiO_2$ impregnated Ni-YSZ anode are fabricated and characterized through current-voltage measurement at different loads. It is shown that the conductivity of porous Ni-YSZ anode and the performance of SOFC button cell with the same anode decreased with the increase in temperature and redox cycling at different time intervals. The power density of 12 % Ni-YSZ anode is 116 $mW/cm^2$ and it increased to 180 $mW/cm^2$ for 4 % $TiO_2$-12 % Ni-YSZ based anodes at 800 °C. Both the cells are tested for 100 h with redox cycles. This increase is interpreted by strong attachment of Ni particles on $TiO_2$ preventing Ni coarsening during prolonged reduction in $H_2$ at 800 °C as observed by SEM. The power density increased with further increase in Ni loading and it reached to 400 $mW/cm^2$ for 4 % $TiO_2$-16 % Ni-YSZ based anodes. The performance increase with addition of $TiO_2$ support in Ni-YSZ based anodes corroborates with the

impedance spectroscopy analyses. Further electrochemical performance of $CeO_2$ and $Nb_2O_5$ impregnated Ni-YSZ anode is analyzed in anode supported SOFC. Cell with 4 % $CeO_2$-11 % Ni-YSZ and 4 % $Nb_2O_5$-11 % Ni-YSZ impregnated anode provided 100 mW/cm$^2$ and 90 mW/cm$^2$ power density, respectively.

Redox cycling of Ni based anode induces cell degradation which limits the cell life time during SOFC operation. In the present study redox testing on electrolyte supported cells has been investigated with $TiO_2$ added NiO-YSZ anode matrix. Button cells are fabricated by die-pressing the YSZ powder as electrolyte and on to which NiO-YSZ or $TiO_2$-NiO-YSZ anode and LSM-YSZ composite cathode are painted. The electrochemical performance stability has been observed by current-voltage characteristics followed by impedance spectroscopy. Anode matrices before and after cell operation have been characterized by X-ray diffraction (XRD), elemental dispersive X-ray (EDX) and scanning electron microscopy (SEM). During cell operation peak power density decreases from 111 mW/cm$^2$ (239 mA/cm$^2$) to 84 mW/cm$^2$ (188 mA/cm$^2$) between 23 to 128 h with five redox cycles for cell having NiO-YSZ (40:60) anode. But for cell with $TiO_2$-NiO-YSZ (10:30:60), anode peak power density was constant and stable around 85 mW/cm$^2$ (194 mA/cm$^2$) throughout the cell run of 130 h and five redox cycles. No loss in open circuit voltage is observed. SEM and XRD studies of $TiO_2$-NiO-YSZ (10:30:60) anodes after cell run points out formation of $ZrTiO_4$, which may be responsible for inhibition of Ni coarsening leading to stable cell performance.

$CeO_2$-NiO-YSZ (10:30:60) and $Nb_2O_5$-NiO-YSZ (10:30:60) anodes materials have been investigated to check the degradation of Ni anode due to coarsening by introducing $CeO_2$ and $Nb_2O_5$. $CeO_2$-Ni-YSZ and $Nb_2O_5$-Ni-YSZ anodes materials are prepared by solid state reaction route and painted on the one side of dense die-pressed

YSZ powder, and co-sintered at 1450 ºC. The other side of pellet was coated with LSM-YSZ cathode sintered at 1250 ºC. The as prepared button cells with $CeO_2$-Ni-YSZ and $Nb_2O_5$-Ni-YSZ anodes showed peak power density 96 mW/cm$^2$ and 127 mW/cm$^2$ respectively in $H_2$ at 800 ºC. Physical characterizations e.g., SEM, XRD, EDX and TEM of above mentioned anode materials are investigated to evaluate the performance of anode materials.

Alternate anode materials like single and bi doped $SrTiO_3$ are synthesized through solid state route and tested in electrolyte supported SOFC. It is observed that after addition of Ni-YSZ (20 wt %) to YST and STN, the performance of the cell improved from 13.68 mW/cm$^2$ to 27.41 mW/cm$^2$ and 6.45 mW/cm$^2$ to 23.52 mW/cm$^2$, respectively. Further bi-doped materials, La, Y and Nb, present both A and B sites of $SrTiO_3$, have been synthesized and tested as anode material for SOFC. The cell performance of bi-doped anode material e.g., LYST and LSTN found to be higher than single-doped anode e.g., LST and STN. As before 20 wt % Ni-YSZ addition to LYST and LNST increased the cell performance from 23 mW/cm$^2$ to 77 mW/cm$^2$ and 25 mW/cm$^2$ to 38 mW/cm$^2$, respectively. LYST-Ni-YSZ anode gave the maximum power density 70 mW/cm$^2$, which is stable for 60 h of operation. The above observations may be explained from EIS and SEM studies showing lower polarization and ohmic resistance and uniform dispersion of Ni in LYST and better connectivity.

# CONTENTS

# List of Figures

# List of Tables