

DEVELOPMENT OF COPPER-CERIA BASED ANODES FOR DIRECT METHANE AND BUTANE SOLID OXIDE FUEL CELLS

GURPREET KAUR



**DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI
MARCH 2014**

DEVELOPMENT OF COPPER-CERIA BASED ANODES FOR DIRECT METHANE AND BUTANE SOLID OXIDE FUEL CELLS

by

GURPREET KAUR

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 2014**

Dedicated to my family

CERTIFICATE

This is to certify that thesis entitled “Development of copper-ceria based anodes for direct methane and butane solid oxide fuel cells” submitted by Mrs. Gurpreet Kaur to the Department of Chemical Engineering, Indian Institute of Technology Delhi is a record of bonafide research work carried out by her. She 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 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.

SuddhasatwaBasu

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 gratitude and heartiest thanks to Prof. Suddhasatwa Basu for his sincere guidance, keen interest and support. 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 by Prof. S. Roy, Prof. A. K. Gupta and Prof. K. K. Pant 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. Rajalekhmi Chockalingam, Ms Jyoti Goel, Mr. Varagunapandiyan N, Mr. Pankaj Kumar Tiwari, Mr. Amandeep Jindal and all other lab members. I would like to thanks Mr. Sunder Singh for his kind support in carrying out experimental runs.

I must express my heartiest thanks to my parents S. Bahadur Singh and Smt. Harjit Kaur for their well wishes. I should not forget my in-laws S. Tara Singh and Smt. Tajinder Kaur who supported me in these years and help me to take challenges through devotion and hard work. I sincerely thank my elder brother S. Harpreet Singh and all other members of my family for their kind support whenever needed.

The research would not have been possible without the support of my husband S. Harminder Singh and daughter Gurnaaz Kaur. I will always be thankful to them for their patience and encouragement to generate positively and strength inside me to accomplish the ultimate goal.

GURPREET KAUR

ABSTRACT

Fuel cells are often perceived as being part of the future solution to the 'energy crisis', providing 'clean' electricity with lesser emission. One of the major requirements of fuel cell is use of hydrogen as a fuel, the oxidation of which takes place at anode. Production of hydrogen by steam reforming reactions of natural gas and higher hydrocarbons require an additional purification steps to satisfy fuel cell demands which increase the cost and complexity of the system. Solid oxide fuel cells are capable of internal reforming of light hydrocarbons such as methane (natural gas), propane and butane, therefore direct oxidation of hydrocarbons is possible. However, carbon deposition is a major concern. The development of anode catalyst materials with improved catalytic and electrochemical properties remains a major research interest. It is required that anode materials should offer greater performance, improved durability and resistance to carbon deposition.

The objective of this thesis is to improve the performance of copper based anodes by studying the electrochemical behavior of Cu/CeO₂-YSZ, Cu-Fe/CeO₂-YSZ and Cu-Co/CeO₂-YSZ anodes in hydrogen, methane and butane fuels. SOFCs are fabricated in laboratory scale using tape casting technique with thickness of < 600 μm and anode porosity of ~70 %. The additives composition (solvents, binders and pore-formers) is optimized to fabricate defect free SOFCs. The wet impregnation method is used for incorporation of CeO₂, Cu, Fe and Co in porous YSZ to prepare the anodes. The prepared anodes are physically characterized by thermal gravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM) and elemental dispersive X-ray spectroscopy (EDX) with elemental mapping. TGA shows the calcination temperature of approximately 300 °C is required to decompose metal (Cu, Co, Fe, CeO₂) nitrates to metal oxides. XRD shows that Cu, Co and Fe metal phases are present in cubic structure after

reduction in H_2 at 800 °C with crystallite size of $\sim 0.15 \mu m$. SEM and elemental mapping shows higher distribution of catalyst particles achieved inside the pores of anodes with addition of Co and Fe in Cu/CeO₂-YSZ anodes, which is useful to provide higher electrical conduction. In this study, current voltage characteristics of prepared anodes are measured for different metal loadings and molar ratios using yttria-stabilized zirconia (YSZ) as electrolyte and strontium doped lanthanum manganate (LSM) as cathode. The maximum power densities of approximately 200 and 320 mW/cm² at current densities of 380 and 520 mA/cm² are observed for Cu-Fe/CeO₂-YSZ anodes with Cu-Fe molar ratio of 1:0 and 1:1 in H_2 fuel at 800 °C. In CH_4 and $n-C_4H_{10}$ fuels, power densities of 120 and 250 mW/cm² at current densities of 240 and 380 mA/cm² are observed for Cu-Fe/CeO₂-YSZ anodes with Cu-Fe molar ratio of 1:1. Cu-Fe/CeO₂-YSZ anodes with Cu-Fe molar ratio of 1:1 showed higher performance in comparison to molar ratio of 1:0 and 3:1. The fitted electrochemical impedance spectra suggests that improved power and current densities of Cu-Fe/CeO₂-YSZ anodes in comparison to Cu/CeO₂-YSZ anodes are due to less ohmic as well as charge transfer resistances in SOFCs. Furthermore, the performance of Cu-Fe/CeO₂-YSZ anodes increases with the increase in temperature, Cu-Fe metal loading and with addition of Pd in Cu-Fe/CeO₂-YSZ anodes. In addition, decrease in power density from 280 to 140 mW/cm² is observed with increase in the anode thickness from 190 to 350 μm due to higher ohmic and concentration polarization in SOFCs.

For continuous 40 h cell operation in H_2 , CH_4 and $n-C_4H_{10}$ fuels, no apparent degradation in performance of Cu-Fe/CeO₂-YSZ anodes is observed. The carbon fibre formation is observed after exposure of $n-C_4H_{10}$ fuel which actually increased the performance of SOFCs due to conductivity provided by carbonaceous species. The reactant gas can reach to surface of the

catalyst through the fibres as well as interstices of the fibres which might be the reason that cells performs for longer period of time. The results suggest that Cu-Fe/CeO₂-YSZ anodes exhibits better stability than conventional Ni-YSZ anodes.

The effect of Cu-Co loading on the performance of Cu-Co/CeO₂-YSZ anodes is further investigated in H₂ and n-C₄H₁₀ fuels at 800 °C. The objectives are to study the micro structural changes and long term stability of Cu-Co/CeO₂-YSZ anodes in n-C₄H₁₀ fuel which has not been reported in literature. Cu-Co/CeO₂-YSZ anodes with Cu-Co loadings of 10, 15 and 25 wt% achieved maximum power densities of 60, 197 and 400 mW/cm² in H₂ and 190, 225 and 275 mW/cm² in n-C₄H₁₀ fuel at 800 °C. During cell operation in n-C₄H₁₀ fuel, total resistance decreased for 10 and 15 wt % Cu-Co loading while it appears to increase for 25 wt % of Cu-Co loading. SEM and TGA suggest that the amount of carbon deposition increases with increase in Cu-Co loadings resulting increase in polarization resistance of cell. The higher amount of carbon formation increases the diffusion resistance and decreases the three phase boundary surface area for the electrochemical oxidation of fuel. HRTEM and EIS suggest that metal particles are detached from the surface of anode by trapping of the catalyst particles in the carbon fibres and thereby decreased the performance of the cell. The performance degradation from 280 to 110 mW/cm² is observed during 16 h cell operation in n-C₄H₁₀ fuel due to increasing amount of carbon deposition with time.

CONTENTS

		Page No.
<i>Certificate</i>		i
<i>Acknowledgements</i>		ii
<i>Abstract</i>		iv
<i>Contents</i>		vii
<i>List of Figures</i>		xi
<i>List of Tables</i>		xxi
<i>Nomenclature</i>		xxii
Chapter 1	Introduction	1-11
1.1	An Overview	1
1.2	High Temperature Solid Oxide Fuel Cells	5
1.3	Motivation and Objectives of Research Work	8
1.4	Organization of the Thesis	10
Chapter 2	Literature Review	12-34
2.1	Anodes of Direct Hydrocarbon Solid Oxide Fuel Cells	12
	2.1.1 Nickel Based Anodes	12
	2.1.2 Copper Ceria Based Anodes	16
	2.1.3 Miscellaneous Anodes	22
2.2	Cathode	26
2.3	Electrolyte	28
2.4	Fabrication Techniques of Anode, Cathode and Electrolyte	30
2.5	Physical and Electrochemical Characterization Techniques	32
2.6	Motivation	33

Chapter 3	Experimental Methods		35-53
3.1	Materials		35
3.2	Fabrication Method of SOFC		36
	3.2.1	Preparation Procedure for Anode and Electrolyte	36
	3.2.2	Preparation Procedure for Cathode	40
	3.2.3	Metal Incorporation in Porous YSZ	42
3.3	Physical Characterization		43
3.4	SOFC Testing		44
3.5	Thermal Gravimetric Analysis of Additives and Sintering		47
3.6	Influence of Different Additives on Tape Casting		49
3.7	Characterization of Cathode		53
Chapter 4	Results and Discussion on Cu-Fe/CeO₂-YSZ Anodes		54-104
4.1	Physical Characterization		55
	4.1.1	Thermal Analysis	55
	4.1.2	X-ray Diffraction	55
	4.1.3	Scanning Electron Microscopy	59
	4.1.4	Elemental Dispersive X-ray	61
4.2	Performance Studies of Cu-Fe/CeO ₂ -YSZ Anodes for Electro-oxidation of H ₂ and CH ₄ Fuels		65
	4.2.1	Effect of Anode Catalyst on the Performance of SOFC in H ₂ Fuel	65

	4.2.2	Effect of Temperature	70
	4.2.3	Effect of Metal Loading and Cell Thickness	71
	4.2.4	Performance of Cu-Fe/CeO ₂ -YSZ Anode in CH ₄ Fuel	77
	4.2.5	Effect of Precious Metal	83
4.3		Performance Studies of Cu-Fe/CeO ₂ -YSZ Anode for Electro-oxidation of n-C ₄ H ₁₀ Fuel	86
	4.3.1	Electrochemical Performance in n-C ₄ H ₁₀ and in H ₂ Fuels	87
	4.3.2	Electrochemical Impedance Analysis	92
	4.3.3	Effect of Temperature on the Performance of Cell in n-C ₄ H ₁₀ Fuel	94
	4.3.4	Effect of Anode Thickness on the Performance of SOFC for C ₄ H ₁₀ Oxidation	94
4.4		Long Term Performance	97
4.5		Conclusions	103
Chapter 5		Results and Discussion on Cu-Co/CeO₂-YSZ Anodes	105-123
5.1		Physical Characterization	106
	5.1.1	Thermal Gravimetric Analysis	106
	5.1.2	X-ray Diffraction Pattern	107
	5.1.3	Elemental Dispersive X-ray Analysis	108
	5.1.4	Scanning Electron Microscopy of fabricated SOFC	108
5.2		Performance of Cu-Co/CeO ₂ -YSZ Anode Based SOFCs	110
	5.2.1	Effect of Loading and Temperature on the Performance of	110

		Cells in H ₂	
	5.2.2	Performance of Cu-Co/CeO ₂ -YSZ Anodes in n-C ₄ H ₁₀ Fuel	114
	5.2.3	Role of Carbon Fibre and Long Term Stability of the Cell	118
5.3	Conclusions		123
Chapter 6	Summary		124-129
6.1	Future Scope		128
	References		130-147
	Appendices		148-156
A1	Composition of additives to obtain different porosities in anode of SOFCs		148
A2	Nernst potential calculation for various fuel oxidation reactions		149
A3	Comparison in performance of Cu/CeO ₂ -YSZ and Cu-Co/CeO ₂ -YSZ anodes		155
A4	Effect of temperature on the performance of Cu-Co/CeO ₂ -YSZ anodes in n-C ₄ H ₁₀ fuels		156
	List of Publications		157-158
	About the Author		159