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

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by

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Submitted

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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.

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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/CeO_2-YSZ, Cu-Fe/CeO_2-YSZ and Cu-Co/CeO_2-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 CeO_2, 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, CeO_2) 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 ~ 0.15 µm. SEM and elemental mapping shows higher distribution of catalyst particles achieved inside the pores of anodes with addition of Co and Fe in Cu/CeO_2-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 magnate (LSM) as cathode. The maximum power densities of approximately 200 and 320 mW/cm^2 at current densities of 380 and 520 mA/cm^2 are observed for Cu-Fe/CeO_2-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/cm^2 at current densities of 240 and 380 mA/cm^2 are observed for Cu-Fe/CeO_2-YSZ anodes with Cu-Fe molar ratio of 1:1. Cu-Fe/CeO_2-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/CeO_2-YSZ anodes in comparison to Cu/CeO_2-YSZ anodes are due to less ohmic as well as charge transfer resistances in SOFCs. Furthermore, the performance of Cu-Fe/CeO_2-YSZ anodes increases with the increase in temperature, Cu-Fe metal loading and with addition of Pd in Cu-Fe/CeO_2-YSZ anodes. In addition, decrease in power density from 280 to 140 mW/cm^2 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/CeO_2-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/CeO_2-YSZ anodes exhibits better stability than conventional Ni-YSZ anodes.

The effect of Cu-Co loading on the performance of Cu-Co/CeO_2-YSZ anodes is further investigated in H_2 and n-C_4H_{10} fuels at 800 °C. The objectives are to study the micro structural changes and long term stability of Cu-Co/CeO_2-YSZ anodes in n-C_4H_{10} fuel which has not been reported in literature. Cu-Co/CeO_2-YSZ anodes with Cu-Co loadings of 10, 15 and 25 wt% achieved maximum power densities of 60, 197 and 400 mW/cm^2 in H_2 and 190, 225 and 275 mW/cm^2 in n-C_4H_{10} fuel at 800 °C. During cell operation in n-C_4H_{10} 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/cm^2 is observed during 16 h cell operation in n-C_4H_{10} fuel due to increasing amount of carbon deposition with time.

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