Synopsis

Renewable energy becomes inevitable for future energy needs. Accordingly, researchers are exploring possible alternatives to conventional fuel based internal combustion engines. In recent years, Bio-fuel (methane/ethanol) based Solid Oxide Fuel Cell (SOFC) is being projected as one of the possible solution to this issue. SOFC converts the chemical energy directly to electrical energy and therefore electrical efficiency as high as 60% can be achieved. Further, higher operating temperature of the SOFC makes it suitable for cogeneration applications whose electrical plus thermal efficiency can reach 80%. Among various SOFC configurations, anode supported planar design is preferred due to relatively low operating temperature. In this case, the ohmic losses can be further reduced as it is possible to use thin electrolyte layer in this design. However, the conventional Ni-YSZ anode is much prone to carburization in presence of hydrocarbon fuels.

The present thesis is devoted to the development of hydrocarbon compatible SOFC anode. Efforts were made to fabricate high performance SOFC using the developed anode.

Chapter-1 introduces the working principle of SOFC, its components and their functionality. Among various designs, planar anode supported SOFC (ASC) is known to have the lowest ohmic losses. The direct internal reforming of hydrocarbon fuels at the SOFC anodes can increase the overall system efficiency. However, the conventional anode of SOFC (Ni-YSZ) is prone to carburization in the presence of hydrocarbons. Hence, the present work was focused towards the development of hydrocarbon compatible anodes for ASC.

Chapter-2 gives an overview about the state-of-the-art anode systems. The state-of-the-art Ni-YSZ anode is prone to carburization in hydrocarbon fuel. Without suitable measures, Ni-YSZ anodes fail just in 25 h of operation in dry CH_4 fuel. There is a gamut of reports on oxide anodes for hydrocarbon fuel. Among the oxide anodes, perovskite manganites and molybdates display better performance. Though the oxide anodes do not face any carburization, their catalytic activity does not match the cermet anode. In fact, the performance of these oxide anodes in hydrocarbon fuel are half of that in H_2 fuel. Cu-based cermet systems are targeted due to the promising carbon retarding ability of Cu atoms. Due to the thermal sensitivity issues, Cu rich compositions have been used only in low temperature fabrication techniques. Most of these compositions are found to be only suitable for electrolyte supported SOFC (ESC) and electrode infiltration techniques. Bimetallic Ni based compositions show better thermal stability and are widely used in ASC. Particularly, Ni-Cu compositions exhibit thermal stability as well as resistance to carburization.

The main objectives of the present study were as follows:

- Development of hydrocarbon compatible anode with the following composition.

  $$M_{1-x}Cu_xYSZ_{1-y}GDC_y$$

  where,

  M → Ni and Co to take care of the electrochemical activity and conductivity

  Cu → To reduce carbon deposition

  YSZ → To match the thermal expansion co-efficient with electrolyte

  GDC →Gadolonia doped ceria to improve the reforming and removal of carbon deposits

  x (0.1-0.8) & y (0.05) are in weight fractions and are optimized to satisfy various critical requirements of SOFC such as thermal stability, conductivity, catalytic activity etc.

- To synthesize the optimized anode composition by a single pot synthesis method such as solution combustion synthesis.
- To fabricate electrolyte supported and anode supported SOFC single cells using the optimized anode composition.
- To characterize the performance of the fabricated SOFC at 800 °C in hydrogen and methane environment.

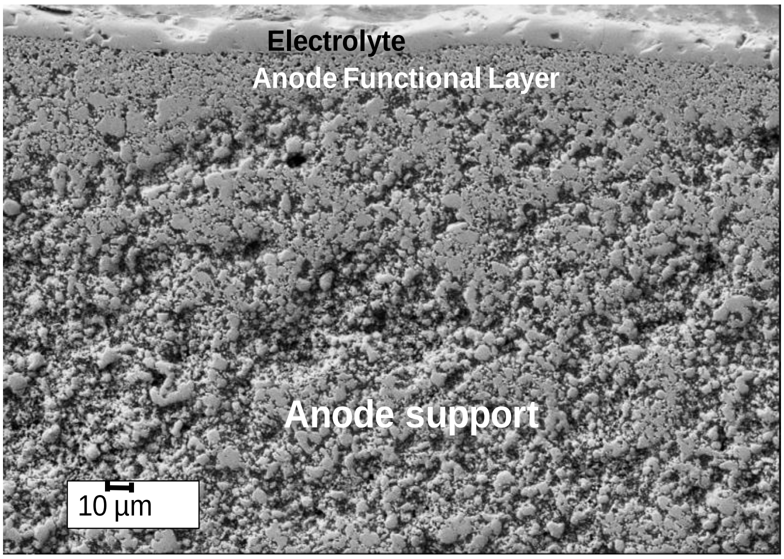
The scope of this study was to derive new SOFC anode composition compatible with hydrocarbon fuel. SOFC with $Ni_{0.9}Cu_{0.1}YSZ_{0.95}GDC_{0.05}$ and $Co_{0.9}Cu_{0.1}YSZ_{0.95}GDC_{0.05}$ anodes were fabricated and systematically explored in H_2 and CH_4 fuels. This work brings out some interesting facts on anode composition with respect to its carburization and electrocatalytic activity. The optimized SOFC anode composition is essential to realize high performance in hydrocarbon fuel. The hydrocarbon compatible SOFC is expected to reduce system complexity and improve the specific power density.

Chaper-3 discusses about the experimental procedures involved in the development of anode composition and SOFC single cells both in ESC and ASC configurations. Tape casting process was utilized to fabricate the anodes. In the anode supported configuration, the anode was co-fired with 10 µm thin electrolyte, whereas in case of electrolyte supported cells, the anode was screen printed over the 2 mm thick electrolyte pellets. Thus fabricated SOFC single cells were subjected to various characterizations such as phase, microstructure, electrical and electro-chemical performances.

In Chaper-4, $Ni_{(1-x)}$-Cu_x-$YSZ_{(1-y)}$-GDC_y anode system was systematically studied and its suitability for SOFC application was established. From the carburization studies, it was evident that $Ni_{0.9}Cu_{0.1}$-$YSZ_{0.95}$-$GDC_{0.05}$ composition had the tendency to reduce the carbon deposition up to 50%. Also, the developed composition was found to have better thermal stability in the typical co-firing process of anode supported SOFC fabrication. Further, $Ni_{0.9}Cu_{0.1}$-$YSZ_{0.95}$-$GDC_{0.05}$ composite anode exhibited an electrical conductivity of 846 S/cm which is reasonably good for SOFC anode. In addition, the electrochemical parameters such as anode impedance and exchange current densities were estimated. The developed ASC had maximum power density of 436 mW/cm^2 at 825ºC under the test conditions available at CSIR-NAL. As this work proved the possibility of fabrication of thermally sensitive Ni-Cu composition without compromising the electro-catalytic activity, it may act as a precursor to evolve high power density cells for hydrocarbon fuels. Thus, the developed anode can replace Ni-YSZ anode in anode supported SOFC for the operation with hydrocarbon.

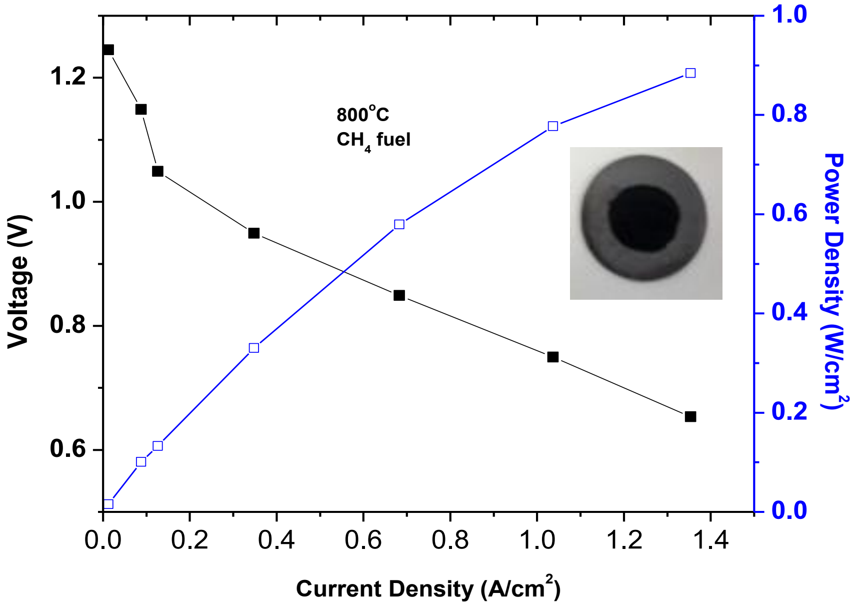
Chapter-5 reports the development of $Co_{(1-x)}$-Cu_x-$YSZ_{(1-y)}$-GDC_y anode composition and performance was analysed in hydrocarbon fuel. $Co_{0.9}$-$Cu_{0.1}$-$YSZ_{0.95}$-$GDC_{0.05}$ displayed good reduction in carbon deposition (67%) reduction in carbon deposition. Also, the alloying of Co with Ni was explored. However, Ni-Co-YSZ had relatively higher carburization than Co-Cu-YSZ-GDC system. Initially, the performance was comparable to $Ni_{0.9}$-$Cu_{0.1}$-$YSZ_{0.95}$-$GDC_{0.05}$ but it degraded quickly in short duration. It was suspected that decreased performance of the cell may be due to segregation and agglomeration of Cu on the surface of Co. Further analysis is required to establish the exact cause of the performance loss.

Chapter-6 reports the effect of synthesis method of $Ni_{0.9}$-$Cu_{0.1}$-$YSZ_{0.95}$-$GDC_{0.05}$ on performance of SOFC in hydrocarbon. There was about 62% reduction in carbon deposition with solution combustion synthesized (SCS) anode and 35% increase in performance was observed when the sintering temperature was reduced from 1300°C to 1250°C. Also, 10% higher performance was observed in SCS anode system in comparison with solid state synthesized anode.



Field emission scanning electron micrograph of the cross-section of $NiO_{0.9}CuO_{0.1}YSZ_{0.95}GDC_{0.05}$ anode supported SOFC with AFL fabricated from solution combustion synthesized powder

The cells with SCS-anode functional layer (AFL) yielded a maximum performance of 884 mW/cm^2 at 800°C in methane fuel. The exchange current density and anode impedance were comparable with standard Ni-YSZ. Thus the synthesized anode composition had excellent electrocatalytic activity while retarding the carburization.



Performance of $Ni_{0.9}$-$Cu_{0.1}$-$YSZ_{0.95}$-$GDC_{0.05}$ ASC with AFL in CH_4 at 800°C

Thus, in the present thesis, $Ni_{(1-x)}$-Cu_x-$YSZ_{(1-y)}$-GDC_y and $Co_{(1-x)}$-Cu_x-$YSZ_{(1-y)}$-GDC_y anode systems have been systematically studied for hydrocarbon fuel. The $Ni_{0.9}$-$Cu_{0.1}$-$YSZ_{0.95}$-$GDC_{0.05}$ anode was found to be suitable for anode supported SOFC in the perspective of carburization resistance and electrochemical performance. The incorporation of tapecasted anode functional layer (AFL) prepared from solution combustion synthesized $Ni_{0.9}$-$Cu_{0.1}$-$YSZ_{0.95}$-$GDC_{0.05}$ anode powder enhanced the performance of anode supported SOFC from 436 to 884 mW/cm^2 in methane fuel.