SYNOPSIS

The thesis entitled ‘Studies on the Chemistry and Processing Techniques of the Electrode and Electrolyte Matrix Materials in Molten Carbonate Fuel Cells (MCFC)’ aims at the study and optimization of the parameters for the preparation of nickel electrodes by aqueous and non-aqueous tape casting processes. This study also focuses on the development of anodes, cathodes and electrolyte retention matrix materials and evaluates their performance in molten carbonate fuel cells.

The Molten Carbonate Fuel Cell (MCFC) is expected to be in use as dispersed power generation device in the future. Significant developments have been reported in literature towards the material selection of the components for MCFC towards the development of prototype MCFC power generators. However, several issues remain unsolved regarding the fabrication of cost effective reliable components for the early commercialization of molten carbonate fuel cells. Keeping this in mind, an attempt has been made in this study to understand the materials involved, their method of preparation and fabrication of various components. The details are described under nine chapters.

Chapter 1 describes the general outline of all the fuel cell systems and the associated thermodynamic aspects of such systems. A brief introduction and the technological status has been given to all the five types of fuel cells namely, alkaline fuel cell (AFC), polymer electrolyte membrane fuel cell / solid polymer fuel cell (PEMFC/SPEFC), phosphoric acid fuel cell (PAFC), direct alcohol fuel cell (DAFC), molten carbonate fuel cell (MCFC) and solid oxide fuel cell / Ceramic fuel cell (SOFC).

A detailed literature review is reported in Chapter 2, which describes the current level of understanding of state-of-the-art components and their fabrication techniques. It is recognized that different methods of fabrication of cell components result in different components with varied performance. The development of porous components with the desired pore structure is the major issue in the practical MCFC development. Therefore, research to identify cost effective and reliable method of fabricating the components with enhanced durability and performance in MCFC is the goal. From the available literature, it is clear that the porous electrodes and matrix materials employed need further improvement in terms of the process of making, mechanical strength, structural integrity, longer life and higher power density.

A research plan has been made and the details are given in Chapter 3. The present research work investigated systematically, the method of fabrication of MCFC components namely, anode, cathode, electrolyte and matrix by tape casting technique and evaluated their
performance in single cell MCFC. This research focuses on the development of Ni electrodes with additives such as Al₂O₃ fiber by tape casting technique, which is not fully addressed till now.

The present study also aims at the physicochemical characterization of these components. This will be helpful in achieving optimized structures for the components, which will have enhanced power output. Finally, single cells were assembled using state-of-the-art and the optimized components through this research study and their performance was investigated with respect to the operating parameters.

The above will be helpful as guidelines for the future.

The various techniques adopted for preparation of materials and fabrication of components during the course of this investigation have been described in Chapter 4. Aqueous tape casting has been adopted to make green nickel sheets using three different types of nickel powders. Polyvinyl alcohol and glycerol were used as binder and plasticizer. A non-aqueous tape casting process involving polyvinyl butyral as binder, polyethylene glycol and benzyl butyl phthalate as plasticizers was also attempted in order to fabricate green nickel sheets with smooth surface. Different tape casting slurry formulations have been made by changing the ingredients' amount in the slurry. Thermo gravimetric analysis (TGA) was used to find out the heating steps involved during sintering.

Anode materials such as Ni-10 wt.% Cr, Ni-Al (5 wt.%) and Ni-LiAlO₂ were used to fabricate green tapes, which were subsequently sintered in flowing hydrogen atmosphere at 850 °C. Lithiated nickel oxide cathode catalyst has been prepared by the solid-state reaction and the characterized using X-ray diffraction technique and particle size analysis. Green electrodes of the same can be prepared by using the aqueous tape casting process, which are either sintered in side the cell or sintered out side the cell. Nickel electrodes containing 5, 10 and 20 wt.% of Li₂CO₃ was also prepared by the aqueous tape casting process and both the green and sintered electrodes were characterized.

Electrolyte retention matrix structures made of γ-LiAlO₂ were prepared by using both aqueous and non-aqueous tape casting processes. Different tape casting slurry formulations were made by changing the ingredients' amount in the slurry. Similarly, pure electrolyte and electrolyte + matrix combined tapes were also prepared by the non-aqueous tape casting process. TGA study was used to find out the burning conditions to be employed during the cell start-up.

Three different cathode materials namely, LiNi₀.₈Co₀.₂O₂, lanthanum strontium cobalt oxide coated nickel oxide and electrode prepared from cobalt coated nickel powder were
prepared by the tape casting process and their solubility in molten carbonate (63/38 Li₂CO₃/K₂CO₃) melt at 650 °C was determined. Atomic absorption spectroscopy (AAS) was used for this study. The electrochemical behavior of the three new cathode materials namely LiNi₀.₈Co₀₂O₂, lanthanum strontium cobalt oxide coated nickel oxide and electrode prepared from cobalt coated nickel powder were studied in an electrochemical half-cell by means of polarization and electrochemical impedance spectroscopy. Laboratory scale 3 cm² cell were assembled using the component prepared in this investigation and the performance of the cell at different temperatures and at different gas flow rates were evaluated.

The results obtained in this investigation are detailed in Chapter 5. Good quality nickel electrode tapes of desired thickness can be prepared form nickel powders by an aqueous tape casting process. The aqueous tape casting process has an advantage over the non-aqueous method in that the slurry employs a biodegradable PVA as the binder. The binder is completely soluble in the solvent namely water. The other additives are also nontoxic in nature. The glycerol is the preferred plasticizer for the aqueous tape casting process. The thickness, the density and packing factor of the nickel tapes depend upon the solid content in the slurry (S/L ~ 50 to 60%). The green tape density values decrease as the binder and plasticizer content increases in the slurry. Good quality porous electrodes can be prepared by sintering these green tapes. The porosity values of 60% can be obtained. Increase of binder and plasticizer content in the slurry is found to increase the porosity of the final sintered electrode. The slurry with a low liquid content produced thick tapes with lower shrinkage factor. These tapes produced thin electrodes with a higher shrinkage factor and porosity after sintering. The data from TGA studies was helpful in optimizing the sintering parameters.

Compared to the aqueous process for making the slurry for processing the LiAlO₂ ceramic powder to form the matrix tapes, the non-aqueous method seems to be a preferable process. The aqueous method yielded tapes with higher thickness and less dense matrix. With non-aqueous slurries, thin tapes with higher shrinkage factor and higher green density could be prepared. The solid content in the non-aqueous slurry is found to be higher than when aqueous slurry is employed. The drying rate is also found to be faster in the non-aqueous method. As expected, in both the cases the green density of the tapes increased as the S/B+P increased. In other words, the density decreased with increase in the total binder. At constant B/S, increase of P/S decreased the green density. At constant P/S, decrease of P/S increased the density. At constant B+P/S, the density is found to depend upon the solid content in the
slurry (S/L). At constant S/L, increase of binder or plasticizer decreased the density and tape strength.

Similarly, good quality electrolyte tapes and electrolyte + matrix tapes could be prepared by the non-aqueous method. The alumina fibre addition to the matrix tapes increased the strength of the matrix. These tapes could be successfully employed for assembling the molten carbonate fuel cell and testing at 650 °C.

A comparison of aqueous and non-aqueous tape casting process has been made. The tape cast green sheet forms the basic building block of complex structures and must meet several requirements during fabrication to enable final high quality and reliable products. These requirements are usually achieved by organic based systems. However, these organic solvents are volatile and irritating and necessitate special precautions concerning inflammability and toxicity. These drawbacks brought to an increasing pressure over the traditional tape casting process and have been encouraged the research towards alternative aqueous based systems which are lower cost and environmentally more friendly. Aqueous tape casting systems have a smaller tolerance to minor changes in processing parameters such as casting composition, drying conditions or film thickness. A non-aqueous suspension dries quickly and produces green sheets having a high density and a fine surface appearance. An aqueous suspension has the disadvantages of high evaporation latent heat and inferior drying characteristics. Non-aqueous solvents have lower boiling points and avoid hydration of the ceramic powder, but require special precautions concerning toxicity and inflammability.

Organic solvent-based slurry is much more volatile and irritating to process but strong uniform green tapes are easy to achieve. It produces crack-free, uniform green tapes only when all variables are controlled extremely well.

Water exhibits a higher surface tension than organic solvents and the solubility of binders in water also limited. Crack-free, uniform green tapes may only be produced using properly optimized water based suspensions under well-controlled conditions. The major disadvantage that has been pointed out for tape casting in water is the slower drying rate to respect organic solvent. Further, slurry formulations for water based tape casting often reveal certain pH instability, high tendency to foaming and premature polymerization. Therefore, producing suitable green tapes strongly depends on a strict control of all these variables making the slurry formulation for water based tape casting process much more problematic than when the solvent is an organic liquid.

Thus the main advantages of switching from an organic solvent-based system to water based system are, reduced health and environmental hazards coupled with a lower cost. The
disadvantages, which have been held against the water based systems, are slow drying, a higher crack sensitivity and, for some materials, reactions with water. However, it is generally easier to obtain slips with high solids loading in water than in systems with organic solvents and this makes it possible to get a fast drying also for water based systems. Hence, it is preferred to adopt aqueous process for the fabrication of the porous electrodes and the non-aqueous process for the fabrication of the matrix and electrolyte structures.

Physical characteristics of the new cathode materials are described in Chapter 6. Three different cathode materials namely LiNiO$_4$Co$_2$O$_2$, lanthanum strontium cobalt oxide coated nickel oxide and electrode prepared from cobalt coated nickel powder were prepared and their physical characteristics were studied. All the three cathode materials showed lower solubility than that of conventionally used nickel oxide in 62:38 mol% Li$_2$CO$_3$/K$_2$CO$_3$ melt at 650 °C under cathode gas condition. The solubilities of the three cathodes are 9 X 10$^6$ nickel mole fraction for LiNiO$_4$Co$_2$O$_2$, 22 X 10$^6$ nickel mole fraction for LSC-NiO and 10 X 10$^6$ nickel mole fraction for cobalt coated nickel electrodes. From the solubility test results it can be safely concluded that use of cobalt doped lithium nickel oxide and cobalt coated nickel electrodes exhibited lower solubility. By improving the physical characteristics such as porosity and pore size distribution of these electrodes MCFC operation with longer lifetime can be achieved.

The electrochemical behavior of the new cathode materials in a half-cell is described in Chapter 7. The impedance behavior of all the three electrodes was similar to that of the conventional lithiated nickel oxide cathode. From half-cell studies, the polarization values of 140 mV for LiNiO$_4$Co$_2$O$_2$, 109 mV for LSC-NiO and 96 mV for cobalt coated nickel electrodes were noticed at a current density of 160 mA/cm$^2$. These results indicated that the performance values for these three materials are lower than that of in-situ lithiated nickel oxide cathode. In spite of the above, in view of better stability of these three cathode materials in molten carbonates at 650 °C, there is scope for improvement. The electrodes made of cobalt coated nickel powder can be a candidate cathode material by achieving the desired porosity and pore size distribution.

This chapter also describes the performance of the prepared components namely, anode, cathode and electrolyte retention matrix in a full cell. A model study has been performed in order to understand the distribution of resistances in the cell components. The partial resistance $R_a$ should be below 0.01 Ω cm$^2$ and $R_a + R_e$ should not exceed 0.3 or 0.4 Ω cm$^2$ (0.1 on the anode and 0.3 on the cathode).
Two case studies have been made and compared. The cases are conceptual and ideal. Case 1 deals with a cell at an OCV of 1.05 V. The cells deliver a voltage of 0.80 V at 200 mA/cm² with a voltage loss of 250 mV and an improved cell will deliver an output of 0.75 V at 300 mA/cm² with a voltage loss of 300 mV. The maximum area specific resistance values are calculated to be 1.25 and 1.0 Ω cm². These values have been chosen from the cell performance value described in recent literature. The total partial resistance due to electronic contacts and electrolyte layer contribute less than 10% of the total loss. The partial resistance due to the anode and cathode are almost in the ratio 1:2. The contribution due to electronic resistance $R_a$ and $R_c$ are also in the same ratio but form 1/3 of the total $R_a$ and $R_c$. The polarization resistance accounts for the remaining 2/3. Again the value on the cathode is higher than on the anode. The voltage loss anticipated on the cathode (150 mV maximum) is at least 2-3 times higher than the anode. These values are the allowable and expected for a cell with optimum performance.

Significant progress has been made in the preparation of porous anodes, cathodes and electrolyte + matrix structures with improved quality, durability and better performance in MCFC cell conditions. Single cell tests with standard 3 cm² area revealed that high current densities (~250 mA/cm²) are achievable. The crack in the matrix was reduced to the minimum by the use of Al₂O₃ fibre for reinforcement and by use of LiAlO₂ powders with two different particle size and surface area. The preliminary results on standard cells indicate that a MCFC cell can be tested with the above characteristics of the components fabricated.

The effect of gas flow rates on the performance of the cell will effectively depend up on the gas flow channel design, its uniformity, gas pressure and gas diffusion characteristics. The effect of gas channel design becomes a critical issue when a bigger size cell is being tested. However, the study made under the present investigation lead to a conclusion that a cell performance of 0.80 V at current densities 200 mA/cm² is achievable in cells with larger area.

The results described in Chapters 5, 6 and 7 have been summarized in Chapter 8. A future scope for further improvements in the components is also discussed. The literature bibliography studied to review the state of art materials and their characteristics for the preparation of electrodes and matrix structures by tape casting technique and to infer the results obtained in the present investigation are arranged in chronological order in Chapter 9.