# CHAPTER 8
SUMMARY AND SCOPE FOR FUTURE WORK

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CHAPTER 8
SUMMARY AND SCOPE FOR FUTURE WORK

8.1. Electrode materials

8.1.1. Aqueous tape casting process

The results described in sections 5.12.1 to 5.1.2.9 indicate that the green density, sintered density, porosity of the electrodes varies as a function of the various organic additives employed in the tape casting process. Good quality nickel electrodes are produced by aqueous tape casting method using PVA as binder and glycerol as plasticizer. The shrinkage factor of the green tape depends on the binder and plasticizer content of the tape casting slurry. High liquidous slurries produced thin tapes with higher packing density and lower porosity. The composition of the binder and plasticizer amount can be controlled to arrive at optimum dense tapes, which can give the desired porosity to the electrodes after sintering. Because of the ease of workability with aqueous slurries, the range of compositions was used for preparing the anodes and cathodes with the respective materials.

8.1.2. Non-aqueous tape casting process

Though the non-aqueous method of preparation of the electrodes yielded good quality electrodes with higher strength, the porosity values are not much higher for the requirement of the MCFC anode and cathode, which should be above 70%. Moreover, non-aqueous method has resulted in nickel sheets of thickness less than 0.5 mm. More experiments have to be carried out to prepare electrodes with optimum thickness of 0.70 – 1.0 mm for the anode and 1.0 – 1.5 mm for the cathode reported in literature. The physical characteristics of the tapes prepared by the non-aqueous method resulted in understanding the behavior of various additives employed in the tape casting process and the binder burn out conditions. On the other hand, the preparation of electrodes by aqueous tape casting technique has resulted in electrodes with thickness greater than 0.5 mm, they are widely adopted for the preparation of the anodes and cathodes which are described in the subsequent sections. However, non-aqueous tape casting method plays a vital role in the preparation of electrolyte, electrolyte + matrix tapes with thickness less than 0.5 mm for use in molten carbonate fuel cells.

Green nickel electrodes with desired physical characteristics could be prepared by keeping the B/P ratio at 0.335 by aqueous tape casting. Non-aqueous tape casting for the preparation of good quality nickel green sheets requires the B/P ratio of 1.111.

Alumina fibre was successfully reinforced into the nickel green sheets prepared by non-aqueous tape casting process. The green density and shrinkage values were considerably reduced which is helpful for the operation of cells with improved performance. Alumina fibre
reinforcement resulted in decrease in the density values will improve the wetting of the electrodes by molten carbonate electrolyte hence cell performance will be increased.

8.1.3. Anode

Anode structures namely Ni-10 wt.% Cr and Ni-Al (5 wt.%) were fabricated by an aqueous tape casting process followed by sintering in hydrogen atmosphere. The density of the sintered electrodes is slightly higher than the density of the green tapes. The shrinkage factor during the sintering process is also below 25%. The porosity of the electrodes are in the range 48 to 60% depending upon the binder, binder + plasticizer and S/L ratios. However, no direct correlations could be observed. The Ni-Cr tapes are sintered at 900 °C as per the sintering schedule described in section 4.4.4. The addition of chromium is mainly to retard the anisotropy in shrinkage of the green tapes and also to retard the dimensional changes occurring in the electrode during their use as anodes in MCFC.

8.1.4. Cathode

Lithiated nickel oxide cathode catalyst was prepared by the solid-state reaction. Particle size analysis revealed that the average particle diameter ranged from 5–100 μm. However, when the particle size distribution is analyzed as a function of particle diameter, more than 80% of the particles are found to be in the range of 5 μm – 30 μm. X-ray diffraction study indicated that all the peaks are corresponding to the nickel oxide with face centered cubic NaCl structure and the peak corresponds to the primary peak of hexagonal type LiNiO₂ at about 2θ = 20° cannot be found. Green tapes were fabricated by the aqueous tape casting process. The green density decreased with increase in the B/B+P ratio for tapes prepared with 9 and 20 wt.% binder concentrations. Whereas at B/S = 30%, the green tape density increased with increase in the B/B+P ratio.

The electrodes were either sintered out side the cell or sintered in-situ during cell operation. Mercury penetration porosimetry study indicated that uniform pore size is observed with pre-sintered cathodes. Electrodes with a total porosity of 75% and the average pore size distribution of around 8.5 microns, which is more suitable as a cathode can be prepared by the aqueous tape casting method. The total penetration volume (pore volume), the average pore diameter, the total pore area and porosity values for the sintered electrodes have significance to the performance as cathodes. The electrodes with higher porosity have higher penetration volume and higher internal pore area (> 5 m²/g).
8.2. Matrix

Compared to the aqueous process for making the slurry for processing the LiAlO$_2$ 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.

Two types of milling processes were optimized for the preparation of γ- LiAlO$_2$ matrix using two different powders. Alumina fibre reinforcement in to the matrix structure will improve the electrolyte holding capacity of the matrix and improved cell performance and low IR drop is expected.

Matrix structure with 1 wt% alumina fibre produced tapes, which are brittle. Alumina reinforcement exceeding 0.5 wt.% produced poor quality tapes due to the agglomerate formation which affected the casting process leaving particles on top surface of the tapes.

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.

8.3. New cathode materials

8.3.1. Lithium Nickel Cobalt Oxide

LiNi$_{0.8}$Co$_{0.2}$O$_2$ showed lower rate of dissolution in molten carbonate under cathode gas conditions when compared to that of NiO. LiNi$_{0.8}$Co$_{0.2}$O$_2$ cathodes for MCFC were made by a tape casting and sintering process. SEM analysis on LiNi$_{0.8}$Co$_{0.2}$O$_2$ electrodes sintered at 800 °C show good pore structure. Electrodes sintered at different temperatures showed different porosity values. The porosity decreased when the sintering temperature increased. Also, electrode sintered at 800 °C had a porosity of 45.1%, which is lower than the value needed for MCFC cathode. The i-V characteristics of LiNi$_{0.8}$Co$_{0.2}$O$_2$ are good offering a
current drain of 160 mA/cm² for a voltage polarization (IR free) of 140 mV. Impedance
spectroscopic studies done on LiNi₀.₈Co₀.₂O₂ under different gas conditions indicate that the
oxygen reduction reaction mechanism follows a positive order for O₂ concentration and
negative for CO₂. This suggests that the oxygen reduction mechanism is qualitatively similar
to that of state-of-the-art cathode listed in literature. Finally LiNi₀.₈Co₀.₂O₂ can be regarded as
an alternate material to the conventional nickel oxide cathodes in molten carbonate fuel cells.

8.3.2. Lanthanum Strontium Oxide coated Nickel Oxide

La₀.₈Sr₀.₂CoO₃ was coated on the state-of-the-art nickel electrode by a sol-gel method.
LSC coating followed by sintering yielded electrodes with good pore structure. There was no
much difference observed in the particle size of the LSC-NiO electrodes after immersion in
molten carbonate for 200 hours. Short-term stability tests in molten carbonate melt at 650 °C
showed that the coating is effective in bringing down the nickel dissolution. The impedance
behavior of LSC-NiO in a half-cell is similar to that of conventional nickel oxide electrodes.
Polarization studies showed 109 mV loss for a current density of 160 mA/cm². However,
extensive pore volume distribution studies need to be done to optimize the pore structure and
porosity, which is expected to give minimum cathode polarization values.

8.3.3. Tape Cast Cobalt Coated Nickel Cathode

Aqueous tape casting process was adopted for the fabrication of cathodes from Co-
coated nickel powders. Sintered electrodes showed lower solubility in molten carbonate at
650 °C when compared to NiO cathode. The electrode showed a polarization of 96 mV for a
current density of 160 mA/cm². Electrochemical impedance studies indicated positive
reaction order for O₂ and negative reaction order for CO₂. Impedance studies after different
time of operation indicated single impedance arc 10 h after reaching the operating
temperature and mass transfer limitations is observed nearly after 20 h. A steady increase in
the impedance values was observed after 82 h. This is due to the loss in electrolyte in the cell.
In all the cases two distinguish arcs are observed; the higher frequency arc is due to the
charge transfer process and the low frequency is due to the mass transfer processes.

Impedance studies after different amounts of electrolyte additions indicated that the
impedance value of the working electrode decreased when increasing the electrolyte addition.
Also, it is evident that at least 30% of the initial weight of the electrolyte has been lost when
operating the cell exceeding 500 hours. It was observed that the half-cell potential did not
change throughout the study indicating the ineffectiveness of the resistance part over the half-
cell potential. This lost in electrolyte quantity may vary in an actual full cell since alumina
housing was used for the present study.
8.3.4. Comparison of three new cathode materials

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 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% Li2CO3/K2CO3 melt at 650 °C under cathode gas condition. The solubilities of the three cathodes are 9X10^-6 nickel mole fraction for LiNi0.8Co0.2O2, 22X10^-6 nickel mole fraction for LSC-NiO and 10X10^-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 three new cathode materials namely LiNi0.8Co0.2O2, lanthanum strontium cobalt oxide coated nickel oxide and electrode prepared from cobalt coated nickel powder were studies in an electrochemical half-cell by means of polarization and electrochemical impedance spectroscopy. The impedance behavior of all the three electrodes was similar to that of the conventional lithiated nickel oxide cathode. The polarization studies showed 140 mV for LiNi0.8Co0.2O2, 109 mV for LSC-NiO and 96 mV for cobalt coated nickel electrodes for a current density of 160 mA/cm^2. These results indicated that the three materials are inferior to lithiated nickel oxide cathode. Though the electrodes exhibited higher polarization values, electrodes made of cobalt coated nickel powder can be a candidate cathode material by achieving the desired porosity and pore size distribution. From the results it can be safely concluded that addition of cobalt either by doping it in a nickel lattice or by means of electroless coating, the solubility level can be minimized.

8.4. Electrochemical studies

The performance of the prepared components namely, anode, cathode and electrolyte retention matrix in a full cell has been made 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 $R_\text{q}$ should be below 0.01 Ω cm^2 and $R_\text{a} + R_\text{c}$ 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. 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/cm^2 with a voltage loss of 250 mV and an improved cell will deliver an output of 0.75 V at 300 mA/cm^2.
with a voltage loss of 300 mV. The maximum area specific resistance values are calculated to be 1.25 and 1.0 Ω cm$^2$. 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 to the 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 cm$^2$ area revealed that high current densities (~250 mA/cm$^2$) are achievable. The crack in the matrix was reduced to the minimum by the use of Al$_2$O$_3$ fibre for reinforcement and by use of LiAlO$_2$ powders with two different particle size and surface area. The preliminary results on standard cells indicate that a multi-cell stack 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/cm$^2$ is achievable in cells with larger area.

8.5. Scope for future work

In this present study, parameters for the fabrication of green nickel electrodes by both aqueous and non-aqueous tape casting processes were optimized. With the knowledge gained from the tape casting process, two types of anodes namely Ni-Cr and Ni-Al, three cathodes namely LiNi$_{0.8}$Co$_2$O$_2$, lanthanum strontium cobalt oxide coated nickel oxide and electrode prepared from cobalt coated nickel powder were also fabricated. Alumina fibre was successfully incorporated into both the nickel and LiAlO$_2$ matrix green tapes during tape casting process. With this experience, the following work will be taken up and done in due course. Multi-layer electrode structure will be the target to achieve electrode with optimum porosity and wetting characteristics.
8.5.1. Preparation of Ni-CeO$_2$ cermet anode

Ni-CeO$_2$ cermet will be prepared by a combustion synthesis and anodes will be made thereafter by tape casting process and tested in a single cell as anode.

8.5.2. Cell testing with developed cathodes

The three new cathode materials namely LiNi$_{x}$Co$_{1-x}$O$_2$, lanthanum strontium cobalt oxide coated nickel oxide and electrode prepared from cobalt coated nickel powder will be tested in a cell as a cathode along with Ni-Cr anode and LiAlO$_2$ matrix. The performance of the cathode materials will be evaluated and further tailoring of physical properties such as porosity and pore size distribution will be carried out in order to select the best cathode material among the three.

8.5.3. Improved matrix development

Lithium aluminate matrix will be prepared from alumina powder, fine aluminium powder and lithium carbonate by a non-aqueous tape casting process using commercial polymer resins such as methyl methacrylate, butyl acrylate. Multilayer tape casting will also be tried to achieve a matrix with flake structure which will have improved physical properties such as porosity and pore size distribution. Thermal cycling of this matrix structure will be performed in order to ensure no crack formation during cell start-up and shut down.

The above future scope of work is expected to improve the single MCFC performance and further study will be useful in assembling multi-cell stacks containing 3-5 cells.