Development and Characterisation of Cathode Materials for the Molten Carbonate Fuel Cell

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Abstract

Among the obstacles for the commercialization of the Molten Carbonate Fuel Cell (MCFC), the dissolution of the state-of-the-art lithiated NiO cathode is considered as a primary lifetime limiting constraint. Development of alternative cathode materials is considered as a main strategy for solving the cathode dissolution problem. LiFeO₂ and LiCoO₂ had earlier been reported as the most promising alternative materials; however, they could not satisfactorily substitute the lithiated NiO. On the other hand, ternary compositions of LiFeO₂, LiCoO₂ and NiO are expected to combine some desirable properties of each component. The aim of this work was to develop alternative cathode materials for MCFC in the LiFeO₂-LiCoO₂-NiO ternary system. It was carried out by investigating electronic conductivity of the materials, first in the form of bulk pellets and then in ex-situ sintered porous-gas-diffusion cathodes, and evaluating their electrochemical performance by short-time laboratory-scale cell operations.

Materials in the LiFeO₂-NiO binary system and five ternary sub-systems, each with a constant molar ratio of LiFeO₂:NiO while varying LiCoO₂ content, were studied. Powders with characteristics appropriate for MCFC cathode fabrication could be obtained by the Pechini method. The particle size of LiFeO₂-LiCoO₂-NiO powders considerably depends on the calcination temperature and the material composition. The electrical conductivity study reveals the ability of preparing LiFeO₂-LiCoO₂-NiO materials with adequate electrical conductivity for MCFC cathode application.

A bimodal pore structure, appropriate for the MCFC cathode, could be achieved in sintered cathodes prepared using poreformers and sub-micron size powder. Further, this study indicates the nature of the compromise to be made between the electrical conductivity, phase purity, pore structure and porosity in optimization of cathodes for MCFC application. Cell performance comparable to that expected for the cathode in a commercial MCFC could be achieved with cathodes prepared from 20 mole% LiFeO₂ - 20 mole% LiCoO₂ - 60 mole% NiO ternary composition. It shows an iR-corrected polarization of 62 mV and a iR-drop of 46 mV at a current density of 160 mAcms⁻² at 650 °C. Altogether, this study reveals the possibility of preparing LiFeO₂-LiCoO₂-NiO cathode materials suitable for MCFC application.

Keywords: molten carbonate fuel cell (MCFC), MCFC cathode, LiFeO₂-LiCoO₂-NiO ternary compositions, electrical conductivity, porous gas diffusion electrodes, polarization, electrochemical performance, post-cell characterization.
Preface

This thesis consists of the background and the experimental procedure for the work carried out on developing LiFeO$_2$-LiCoO$_2$-NiO cathode materials for Molten Carbonate Fuel Cells, together with a summary of the outcome presented in the five appended papers.

*Paper I.*

*Paper II.*

*Paper III.*
**Athula Wijayasinghe**, Bill Bergman and Carina Lagergren, ‘’*A study on LiCoO$_2$-rich cathode materials for the MCFC based on the LiCoO$_2$-LiFeO$_2$-NiO ternary system*’’ Submitted to Electrochemica Acta. (Revised version).

*Paper IV.*
**Athula Wijayasinghe**, Bill Bergman and Carina Lagergren, ‘’*Synthesis and characterization of LiFeO$_2$-LiCoO$_2$-NiO materials for Molten Carbonate Fuel Cell cathodes*’’ Submitted to Ceramics International.

*Paper V.*
**Athula Wijayasinghe**, Bill Bergman and Carina Lagergren, ‘’*Fabrication and characterization of LiFeO$_2$-LiCoO$_2$-NiO cathodes for the Molten Carbonate Fuel Cell*’’ Submitted to Ceramics International.
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# Table of contents

1. **Introduction**  
   1.1. Fuel cells  
      1.1.1. Different types of fuel cells  
      1.1.2. Fuel cell construction  
   1.2. The Molten Carbonate Fuel Cell (MCFC)  
      1.2.1. Design and operation of MCFC  
      1.2.2. Background and current status of MCFC  
   1.3. The MCFC cathode  
      1.3.1. The cathode design  
      1.3.2. Cathode dissolution  
      1.3.3. In solving the cathode dissolution problem  
   1.4. Development of alternative cathodes for MCFC  
   1.5. Objective of the work  

2. **Experimental Procedure**  
   2.2. Material preparation and characterization  
      2.1.1. The glycine-nitrate method  
      2.1.2. The Pechini method  
      2.1.3. Calcination of powder  
      2.1.4. Characterization of powders  
      2.1.5. Preparation and characterization of sintered materials  
      2.1.6. Electrical conductivity measurements on sintered pellets  
   2.2. Cathode fabrication and characterization  
      2.2.1. Powder synthesis for cathode preparation  
      2.2.2. Tape casting  
      2.2.3. Cathode sintering  
      2.2.4. Preliminary characterization of sintered cathodes  
   2.3. In-cell testing of prepared cathodes  
      2.3.1. The laboratory cell unit  
      2.3.2. Polarization measurements  
      2.3.3. Post-cell characterisation  

3. **Results and Discussion**  
   3.1. Materials study  
      3.1.1. Feasibility of powder preparation methods  
      3.1.2. Phase analysis of prepared materials  
      3.1.3. Electrical conductivity of prepared materials  
   3.2. Cathode fabrication study  
      3.2.1. Powder for cathode preparation  
      3.2.2. Porous gas diffusion cathodes  
      3.2.3. Phases present in sintered cathodes  
      3.2.4. Pore structure of cathodes  
      3.2.5. Electrical conductivity of cathodes  
      3.2.6. Selection of cathodes for cell testing
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3.</td>
<td>Electrochemical performance study</td>
<td>29</td>
</tr>
<tr>
<td>3.3.1.</td>
<td>Common trends observed in cell studies</td>
<td>29</td>
</tr>
<tr>
<td>3.3.2.</td>
<td>Electrochemical performance of cathodes</td>
<td>31</td>
</tr>
<tr>
<td>3.3.3.</td>
<td>Post-cell characterization of cathodes</td>
<td>34</td>
</tr>
<tr>
<td>4.</td>
<td>Concluding remarks</td>
<td>37</td>
</tr>
<tr>
<td>5.</td>
<td>Suggestions for future work</td>
<td>38</td>
</tr>
<tr>
<td>6.</td>
<td>References</td>
<td>39</td>
</tr>
</tbody>
</table>

Appendix Paper I - V
1. Introduction

A brief introduction to the basic principles, construction and common types of fuel cells, is presented at the beginning of this section. Thereafter, a brief description of the Molten Carbonate Fuel Cell (MCFC) is given by focusing mainly on its cathode and the dissolution of the state-of-the-art-cathode material. Finally, the background and the current status of the cathode development work are presented. If nothing else is mentioned, the concepts presented in this introduction part are from the references [1-8].

1.1. Fuel cells

Fuel cells are electrochemical devices, which convert chemical energy of electrochemical reactions directly into electrical energy. Therefore it is a more efficient way of power generation than most of the conventional power generation systems, which involve thermal or mechanical energy as intermediates. The increasing demand for energy as well as preserving the global environment have made it more and more important to develop such energy systems with high-energy conversion efficiency and very low environmental pollution.

![Figure 1.1. A schematic representation of the operation of a single fuel cell unit.](image)

The basic physical structure or building block of a fuel cell consists of an electrolyte layer in contact with a porous anode and a porous cathode on either side. In a typical fuel cell, fuel (usually hydrogen or light hydrocarbons) is fed continuously to the anode compartment and an oxidant (usually oxygen from air) is fed continuously to the cathode compartment. The electrochemical reactions take place at the electrodes producing an electric current through the external load. A schematic representation of a fuel cell with the reactant/product gases and the ion conduction flow directions through the electrolyte is shown in Figure 1.1.

A fuel cell, although having components and characteristics similar to those of a typical battery, differs much in the way of operating. A battery is an energy storage device, in which the maximum energy available is determined by the amount of chemical reactant stored within the battery itself. On the other hand, a fuel cell has the capability of producing electrical energy for as long as the fuel and the oxidant are supplied to the electrodes. However, in reality, degradation, primarily corrosion, or malfunction of components limits
the durability of fuel cells. Most of these drawbacks are, to a great extent, associated with the properties of the materials used in cell components.

### 1.1.1. Different types of fuel cells

A variety of fuel cells are in different stages of development and the most common classification of fuel cells is by the type of electrolyte used in the cell.

**Table 1.1. The most common types of fuel cells.**

<table>
<thead>
<tr>
<th>Name</th>
<th>Electrolyte</th>
<th>Operating temperature (°C)</th>
<th>Charge carrier</th>
<th>Catalyst</th>
<th>Prime cell components</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaline Fuel Cell</td>
<td>Liquid KOH</td>
<td>65 - 220</td>
<td>OH⁻</td>
<td>Platinum</td>
<td>Carbon based</td>
</tr>
<tr>
<td>Phosphoric Acid Fuel Cell</td>
<td>Liquid H₃PO₄</td>
<td>200</td>
<td>H⁺</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Polymer Electrolyte Fuel Cell</td>
<td>Ion exchange membranes</td>
<td>80</td>
<td>H⁺</td>
<td>&quot;</td>
<td>Graphite based</td>
</tr>
<tr>
<td>Molten Carbonate Fuel Cell</td>
<td>(Li₂,K₂)CO₃ melt</td>
<td>650</td>
<td>CO₃²⁻</td>
<td>Nickel</td>
<td>Stainless steel based</td>
</tr>
<tr>
<td>Intermediate Temperature Solid Oxide Fuel Cell</td>
<td>Ceramic</td>
<td>600-800</td>
<td>O²⁻</td>
<td>Perovskites</td>
<td>Ceramic</td>
</tr>
<tr>
<td>Tubular Solid Oxide Fuel Cell</td>
<td>Ceramic</td>
<td>800-1000</td>
<td>O²⁻</td>
<td>Perovskites</td>
<td>Ceramic</td>
</tr>
</tbody>
</table>

### 1.1.2. Fuel cell construction

Generally, fuel cells are constructed according to a planar design for ease of manufacturing of single components and of assembling them into a cell. The combined thickness of electrodes and electrolyte is typically of about a few millimeters. In a planar design, a series connection can easily be accomplished by stacking individual cells with bipolar plates in between. The bipolar plate provides the electrical contact between the anode of one cell and the cathode of the adjacent cell while keeping their process gases separated.

The electrodes are electronic conductors with high porosity, which is desired for maximizing the electrocatalytic surface area and to enable transport of process gases to the catalytic sites. In these porous gas diffusion electrodes, the electrochemical reactions take place at the interface of reactant gases, catalyst and electrolyte. Therefore, a sufficient contact area of these three phases has to be provided in this respect. The electrolyte, apart from being an electrical insulator and ionic conductor, should also act as a gas barrier between the electrodes. Operating fuel cells produce direct current with current densities, in general, of several hundreds of mAcm⁻². Single cell voltages are generally in the range of 0.5 - 1 V, therefore, single cells are connected in series for practical purposes.

### 1.2. The Molten carbonate fuel cell (MCFC)

#### 1.2.1. Design and operation of MCFC

The MCFC uses a salt mixture of alkali carbonates as the electrolyte, which provides mass and charge transfer through carbonate ions from the cathode to the anode. The electrolyte currently used by most developers, is a mixture of lithium carbonate and potassium carbonate.
Besides, mixtures of lithium carbonate and sodium carbonate, and carbonates of alkaline-earth metals are also being used. The operating temperature of a typical MCFC is around 650 °C, and the high operating temperature is necessary to achieve sufficient conductivity of its carbonate electrolyte. At 650 °C, the carbonate mixture is in the molten state and becomes a good ionic conductor. The molten electrolyte is contained in a porous electrolyte matrix of LiAlO₂, which is an electrically insulating and chemically inert ceramic. An advantage associated with the high operating temperature is that noble metal catalysts are not required for MCFC. Instead, nickel and nickel oxide can be used for the anode and the cathode respectively. A schematic representation of a typical MCFC is given in Figure 1.2.

Figure 1.2. A schematic representation of a typical MCFC.

The MCFC anode operates under a reducing atmosphere at a potential typically 700 to 1000 mV more negative than that of the cathode. Several transition metals are stable in molten carbonate and are suitable as electrocatalyst for hydrogen oxidation under these conditions. A typical MCFC uses nickel-chromium alloy as the anode material. The additive, chromium in the form of dispersed oxides, to metallic nickel enhances the long-term stability of the anode with respect to sintering and creeping.

In the MCFC, the oxidizing agent for hydrogen is CO₃²⁻, which is formed at the cathode and transported to the anode through the electrolyte. Therefore, CO₂ is added to the cathode feed gas and the CO₂ is again liberated at the anode. In practice, CO₂ is provided by recycling the anode off-gas to the cathode. The anode process comprises of a reaction between hydrogen and CO₃²⁻, which is obtained from the electrolyte.

Therefore the main electrode reaction at the anode is oxidation of hydrogen, which is the principal reactant in the fuel gas:

\[
\text{H}_2 + \text{CO}_3^{2-} \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2\text{e}^- \quad (1.1)
\]

The reaction products of the anode are water and carbon dioxide, while electrons are released to the external circuit from the anode.
On the other side of electrolyte, the cathode process involves a reaction between oxygen and carbon dioxide, obtaining electrons through the external circuit. The carbonate ions, which are the reaction product of the cathode, enter the electrolyte. Hence, the overall electrode reaction at the cathode is the reduction of oxygen and \( \text{CO}_2 \), which are the reactants in the oxidant gas:

\[
\frac{1}{2}\text{O}_2 + \text{CO}_2 + 2e^- \rightarrow \text{CO}_3^{2-} \quad (1.2)
\]

Therefore the net electrochemical reaction is the oxidation of hydrogen with the transfer of two electrons from anode to cathode:

\[
\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} \quad (1.3)
\]

At the anode, other fuel gases such as \( \text{CO} \), \( \text{CH}_4 \) and higher hydrocarbons can be oxidized by conversion to \( \text{H}_2 \). Although direct electrochemical oxidation of \( \text{CO} \) is possible, it occurs very slowly compared to that of hydrogen. Therefore oxidation of \( \text{CO} \) is mainly carried out via the water-gas shift reaction, which equilibrates very rapidly at the MCFC anode environment:

\[
\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \quad (1.4)
\]

The direct electrochemical oxidation of \( \text{CH}_4 \) and other higher hydrocarbons are negligible. As a result, they are steam-reformed in a separate reformer (external reforming) or in the MCFC itself (internal reforming).

**1.2.2. Background and current status of MCFC**

The concept of the MCFC dates back to the late 1940s, and the first MCFCs were demonstrated by Broers and Ketelaar in the 1950s. However, the operation of the first pressurized MCFC stacks was taken place in the early 1980s and the development of the MCFC technology has been relatively slow. A strong incentive for its development as a utility fuel cell did not exist until the early 1970s and its effectiveness and reliability were not demonstrated until later in that decade. The high operating temperature, the corrosivity of the molten salt and the rather complicated electrode processes of the MCFC put many obstacles in the way of a rapid development.

After having been under study and development for more than half a century, the MCFC is approaching the early stages of commercialization [9-12]. MCFC technology has already entered the 0.1- 2 MW demonstration phase for verification of initial performance and efficiency, and for obtaining operating experience. Though the start-up, testing and operation have been carried out in several pilot plants [12-17] a very few number of single MCFCs has been reported of long-term operations [18]. Most of demonstrations did not last for more than 10,000 hours and it is mainly due to the relatively high solubility of metal oxides in the aggressive melt that causes serious troubles.

It is generally assumed that a stack lifetime of at least 40,000 hours is required in order to achieve cost of electric targets, provided that the system is used for co-generation [19]. It is well known that the lifetime limiting issues for MCFC systems are mainly materials issues of the stack. Dissolution of NiO cathode material, corrosion of separator plates, electrolyte losses, electrolyte retention capacity, catalyst deactivation (in the case of internal reforming), matrix cracking, high temperature creep of porous components and contaminants are the main lifetime limiting constraints [19, 20]. Therefore improvement in endurance of the MCFC
stack and its components is an important issue in the worldwide research and development of MCFC.

In spite of the technical difficulties in its development, the MCFC has undeniable advantages, which are mainly connected with the higher operating temperature, such as high electrical efficiency, the possibility of using natural gas without external reforming and the high-grade waste heat generated. These characteristics allow a wide spectrum of applications for the MCFC, varying from central power generation to industrial or commercial co-generation. In addition, the MCFC is insensitive to CO$_2$ and immune to poisoning by CO, both of which are contained in fuel gases derived from fossil fuels. Under the operating conditions of the MCFC, CO is oxidized via the water-gas shift reaction to CO$_2$ with the production of hydrogen.

1.3. The MCFC cathode

The MCFC uses a porous gas diffusion cathode whose porous structure allows extensive contact between reactant gases, molten electrolyte and the electronically conducting electrode material. The pore structure of the cathode is designed to supply a three-phase zone as large as possible, to facilitate more reaction sites for the cathode reaction. A schematic representation of the three-phase zone of the MCFC cathode is given in Fig 1.3.

![Figure 1.3. A schematic representation of the three-phase zone of the MCFC cathode.](image)

In general, molten carbonate is an extremely corrosive medium, but the stability of specific metals and alloys depends strongly on the gas atmosphere. Only a few noble metals are stable under an oxidizing atmosphere such as air or oxygen-CO$_2$ mixtures. Therefore, from the viewpoint of cost, semiconducting oxides are the only practical cathode materials for the MCFC. The lithiated nickel oxide has been the best choice for the MCFC cathode material since the 1970s. The state-of-the-art cathode, generally formed from porous nickel by in situ oxidation and lithiation during cell start-up, possesses good electrocatalytic activity and electronic conductivity at the operation conditions.
1.3.1. The cathode design

The cathode structure has been recognized as one of the principle factors determining the performance of the MCFC. The cathode material should fulfil a number of requirements such as thermal and chemical stability together with better resistance to sintering, swelling, creep and failure, under working conditions [21, 22]. Moreover, the cathode material should possess adequate electrical conductivity and this property should not negatively affect the performance of the cathode in the electrochemical cell. In addition, the material should be able to fabricate into porous electrodes with sufficient mechanical strength and high specific surface area.

Generally, the state-of-the-art lithiated NiO cathode is fabricated starting with nickel plaques, which typically have a preoxidation porosity of 70 - 80% and a mean pore size of 10 \( \mu \)m [5, 23]. The lithiation and oxidation occurs spontaneously when nickel is in contact with the molten electrolyte, containing lithium carbonate, under an oxidizing atmosphere, during initial cell operation. Upon the in situ lithiation and oxidation, the porosity decreases to 55 - 65 % with a median pore size of 5 -7 \( \mu \)m. Further, the lithiation of the in situ formed NiO results in an uptake of approximately 2 atomic% of Li, which can enhance the electronic conductivity up to about 5 S/cm under operation conditions. It is also possible to fabricate NiO cathodes ex-situ from nickel oxide powders.

During lithiation and oxidation, the microstructure changes to form agglomerates of mostly very small NiO particles. The micro (< 1 \( \mu \)m) pores between these individual NiO particles, provide an extended reaction surface as well as a cross-sectional area for the ionic conduction path. This microporosity is an essential feature for good wetting of the cathode by the electrolyte. On the other hand, the agglomerates formed in the cathodes are separated by gas-filled channels or macro (> 1\( \mu \)m) pores, which corresponds to the pores of the original nickel plaque. These macro pores remain open and provide a cross-sectional area for the diffusion of gas into the interior of the electrode.

Thus, a typical lithiated NiO cathode comprises such a critical bimodal pore size distribution composed of appropriate micro and macro pores. Including diffusional and ohmic polarization losses, the porous lithiated NiO cathode is projected to cause about 100 mV total polarization loss at 160 mA cm\(^{-2}\). However, further reduction in total polarization loss is desired in achieving commercial state for MCFC.

1.3.2. Cathode dissolution

A typical MCFC operates at 650 °C under atmospheric pressure (1 atm) producing a current density of 160 mA cm\(^{-2}\) at a voltage of about 0.75 V. Under these operation conditions, the NiO cathode material, which reacts with CO\(_2\) present in the cathode, is subjected to a low and continuous dissolution process when it is in contact with the carbonate electrolyte.

A proposed acidic dissolution mechanism [5, 20, 24] can be presented as follows:

\[
\text{NiO} + \text{CO}_2 \rightarrow \text{Ni}^{2+} + \text{CO}_3^{2-} \quad (1.5)
\]

The dissolved Ni\(^{2+}\) diffuses under a concentration gradient towards the anode side through the electrolyte-matrix structure. The diffusing Ni\(^{2+}\) reduces to metallic Ni by reacting with hydrogen, which diffuses to the matrix from the anode:

\[
\text{Ni}^{2+} + \text{H}_2 + \text{CO}_3^{2-} \rightarrow \text{Ni} + \text{CO}_2 + \text{H}_2\text{O} \quad (1.6)
\]
The reduced metallic Ni precipitates in the electrolyte structure between the two electrodes. This continuous dissolution of cathode material, results in a loss of cathode mass with a reduction of the surface area available for electrochemical oxygen reduction. Further, the precipitation of metallic nickel particles in the matrix will eventually cause short-circuiting of the cell before the designed lifetime [25]. Therefore the cathode dissolution has been regarded as the primary lifetime limiting constraint of the MCFC, particularly under pressurized operations. [6, 18].

Moreover, according to Equation 1.2, a higher partial pressure of CO₂ in the cathode gas is required in order to produce a higher current density. However, according to Equation 1.5, the rate of Ni²⁺ transport towards the anode increases with increasing CO₂ pressure due to an increased solubility of nickel oxide in the molten carbonate electrolyte. Then the cathode dissolution is accelerated reducing the lifetime of the cell further. Hence, the dissolution is more critical especially in producing higher current densities with high partial pressures of CO₂. Hence, in order to achieve the lifetime of 40,000 hours, which is a development goal in an MCFC commercial system, the dissolution of cathode should be diminished.

1.3.3. In solving the cathode dissolution problem

To overcome the cathode dissolution problem, several different approaches have been put forward and investigated by many developers during the last few decades. The shorting time (time to short-circuit the cell) has been found to be proportional to matrix thickness and inversely proportional to the CO₂ partial pressure. Also the nickel content deposited in the matrix is a function of the CO₂ partial pressure. Accordingly, suppressing of cathode dissolution by adjusting these conditions has earlier been studied to overcome this adverse effect. Several efforts were made by lowering the partial pressure of CO₂ in cathode gas to reduce the dissolution of NiO. In addition, some attempts were carried out to delay the short-circuiting of the cell by increasing the thickness of the matrix [5, 25]. By doing so, the cathode dissolution could be reduced to some extent; however, at the same time those endeavors adversely affected the performance of the cell. Further, this approach has shown a very limited effect in reducing the dissolution of the NiO cathode.

Besides from adjusting the operating conditions, two other main approaches have been put forward to overcome the cathode dissolution problem during the last three decades. The reduction of the dissolution of nickel oxide through changing the composition of the molten salt is one such approach of solving the dissolution problem [26-32]. The other strategy is the development of suitable alternative cathodes to replace the state-of-the-art NiO cathode [25, 33-78].

Since it is generally agreed that the NiO cathode dissolution takes place by acidic mechanism, the acidic dissolution is supposed to decrease by increasing the basicity of the molten carbonate. More basic carbonate melts, either by increasing the content of Li₂CO₃ in the state-of-the-art electrolyte (62 mole% Li₂CO₃ + 38 mole% K₂CO₃) or by substituting Na₂CO₃ for K₂CO₃, have been studied to increase the basicity. The studies on Li/Na carbonate eutectics showed the ability of decreasing the Ni dissolution rate in the melt [28-32]. The 52 mole% Li₂CO₃ + 48 mole% Na₂CO₃ carbonate eutectic is regarded to be a promising lithium containing eutectic for the MCFC application. Although, there is disagreement of the objective of using Li/Na carbonate eutectic instead of Li/K carbonate eutectic [30], a number of current investigations are going on with Li/Na carbonate eutectics.
Moreover, both the Li/K and Li/Na carbonates have been further investigated by adding alkaline earth ions such as Mg, Ca, Sr and Ba to the melts [26-28]. Small amounts of alkaline-earth carbonate to the eutectic could reduce the dissolution rate to some extent without degrading the cell performance, however, larger amounts considerably reduced the cell performance. Although adjusting the basicity of electrolyte reduces the solubility of NiO to some extent, this approach so far has shown a limited effect in reducing the dissolution of the NiO cathode [30].

1.4. Development of alternative cathodes for MCFC

Developing of alternative cathodes for MCFC has mainly been carried out by either modifying NiO or identifying alternative cathode materials, which have longer lifetime in the melt. In searching for new cathode materials for MCFC, the emphasis should be mainly given to the stability of the candidate materials under MCFC working conditions. Lower solubility of the material in the cathode environment and higher solubility at the anode environment than lithiated NiO, is much preferable. Moreover, the candidate material should posses adequate electrical conductivity (> 1 S/cm at 650 °C) for proper electrical conduction. High electrocatalytic activity for the O₂ reduction and suitability for fabrication into porous electrodes structures with high specific surface area are other important requirements [33, 34].

In the early 1980s, some thermodynamically stable, potentially conductive compounds containing ions, which can exist in multiple valence states, were evaluated for alternative cathode materials. Basically, the compounds that contain multivalent ions have the potential for electronic conductivity due to intrinsic nonstoichiometry or by further enhancement of conductivity through doping. Screened from electrical resistivity and solubility testing, the materials, LiFeO₂, LiCoO₂ and LiMnO₃, which are not easily reduced or decomposed at the anode environment, were identified as promising candidates [6, 34, 35].

Of these three candidates, LiCoO₂ has been studied most extensively [26, 34-46]. Though LiCoO₂ possess lower electrical conductivity than NiO, the conductivity (about 1 S/cm at 650 °C) is adequate to select LiCoO₂ as a candidate for the MCFC cathode. Further enhancement of the conductivity can be done by increasing the Li/Co ratio, between 1.08 and 1.35. Doping with acceptors such as Mg can also enhance the electrical conductivity as well as the exchange current density.

However, LiCoO₂ dissolves at high partial pressures of CO₂ analogous to NiO [26]. Transport rate for cobalt-containing species to the anode is expected to be lower than that for NiO due to the lower solubility of LiCoO₂ in the (Li,K)₂CO₃ melt [39]. However, at the anode, the dissolved cobalt ions are reduced to metallic cobalt and may lead to poor MCFC performance and eventual short-circuiting. Cell studies with optimized LiCoO₂ cathodes showed an electrochemical performance comparable to that of the lithiated NiO cathodes. However, the contact resistance between current collector and LiCoO₂ cathodes is 3-4 times larger than that with lithiated NiO cathodes [21, 37, 38]. Low mechanical strength of porous LiCoO₂ cathodes and high cost of LiCoO₂ compared to NiO, and especially to LiFeO₂, have further limited the practical use of LiCoO₂ in MCFC stacks.

On the other hand, LiFeO₂ showed a negligible solubility at the working environment and the transport of LiFeO₂ across the electrolyte appears to be zero [26]. Also in contrast to Ni²⁺ and Co²⁺, the Fe²⁺ is not reduced at the anode. The stoichiometric oxide (Li/Fe = 1) show very low electrical conductivity of about 3x10⁻³ S/cm in cathode gas (30% CO₂ + 70% air) at 650
°C, however, the conductivity can be increased with increasing Li content (1.3 x10\(^{-1}\) S/cm for Li/Fe = 1.04). Yet, the conductivity enhanced either by excess Li or by doping with other cations, has not been adequate for using LiFeO\(_2\) as a direct substitute for the lithiated NiO [26, 35, 46-49]. Also the exchange current density for oxygen reduction reaction on LiFeO\(_2\) is about two orders of magnitude lower than that of NiO. This slow kinetics for oxygen reduction further limited the possibilities of improving LiFeO\(_2\) as a cathode material for MCFC.

LiMnO\(_3\) shows a comparable low solubility to that of LiFeO\(_2\), however, the conductivity of undoped LiMnO\(_3\) is very low, about 1.4 x10\(^3\) S/cm at 650 °C [35]. Though doping can enhance the conductivity, the increase of conductivity with dopants is not adequate to use them for the MCFC cathode.

Accordingly, most of the investigations with single-phase candidate materials failed because of their low electronic conductivity or poor oxygen reduction kinetics. The approach of developing alternative cathodes for MCFC has since been diverted to either modifying NiO or, improving earlier proposed alternative single candidates by doping or forming into mixed oxides.

Under the modification of NiO, a considerable amount of research work has been performed on surface modification of NiO cathodes with more dissolution resistant materials. NiO cathodes coated with LiCoO\(_2\), LiFeO\(_2\) or La\(_{0.1}\)Sr\(_{0.2}\)CoO\(_3\) have shown the ability of reducing the solubility of NiO in the carbonate melt [50-55]. Also NiO cathodes modified with cerium, lanthanum and cobalt have recently been studied [56-59]. In most of these studies, it has been found that the surface modified electrodes performed better than lithiated NiO in dissolution studies.

Apart from above mentioned surface modification of NiO cathodes, there have been a number of different approaches on modifying NiO based cathode materials. High lithium content lithium-nickel oxides, Li\(_x\)Ni\(_{1-x}\)O (x > 0.2) have been studied and these studies showed some promising characteristics [60-62]. In addition, ceramic composites such as NiO/CoO, CoO/Ni and MgFe\(_2\)O\(_4\)/Ni [63-66], and alloys such as nickel-niobium, nickel-aluminum and nickel-titanium [67-69] have also been investigated for the MCFC cathode application.

Possibilities of stabilizing NiO with different additives such as alkaline earth oxides, cobalt, cadmium, zinc, copper and iron [70-73] has already evaluated. Moreover, cobalt substituted lithium-nickel oxides and Ni powder particles coated by Co are some of the modified NiO based materials recently studied for cathode preparation [65, 74]. Furthermore, the possibility of using NiO/LiCoO\(_2\) double layer cathodes has also been evaluated [75]. Though many of the modified NiO cathodes have shown better resistance to dissolution, none of them could successfully substitute the state-of-the-art lithiated NiO cathode.

On the other hand, possibility of improving alternative single candidates, such as LiFeO\(_2\) and LiCoO\(_2\), by doping or forming into mixed oxides has also been investigated. Doping LiFeO\(_2\) with different additives such as Co, Mg and Mn [49] showed the possibility of improving the electrical conductivity. In a comparative study of lithiated NiO, Co-doped LiFeO\(_2\) and LiCoO\(_2\) cathodes, Makkus et al. [76] proposed of having the same reaction mechanism for oxygen reduction for these three cathodes. It indicates that the electrochemical behavior is similar and the different performances in the MCFC are due to differences in electrical conductivity,
specific surface area, chemical stability, etc. Therefore it was suggested that a mixture of these oxides should combine the desirable properties of each single candidate, hence forming a better material. Kudo et al [77] reported the performance of in-situ formed Ni-Fe-Co oxides in Li/Na carbonate eutectic. With their solubility studies performed on these ternary oxides, they showed the decreasing of Ni$^{2+}$ solubility in the carbonate melt with the increasing of Fe content of the ternary oxide.

Bloom et al [78] were to first propose a phase diagram for the LiFeO$_2$-LiCoO$_2$-NiO ternary system, by extrapolating their experimental data obtained from certain ternary compositions prepared by mixed-oxide route or glycine-nitrate method. Based on their electrical resistivity measurements performed on selected ternary compositions, under different CO$_2$ partial pressures, they suggested low resistivity and low sensitivity to CO$_2$ for these ternary compositions. Further, their cell test performed with an in-situ sintered cathode prepared from 75 mole% LiFeO$_2$-12.5 mole% LiCoO$_2$-12.5 mole% NiO ternary composition, indicated that ternary compositions of LiFeO$_2$, LiCoO$_2$ and NiO possessing adequate electrocatalytic activity. Hence the LiFeO$_2$-LiCoO$_2$-NiO materials were proposed as more viable alternatives to lithiated NiO [6, 78-81].

1.5. Objective of the work

Ternary compositions of LiFeO$_2$, LiCoO$_2$ and NiO are expected to combine some desirable properties of each component. LiCoO$_2$ and NiO are expected to enhance the electrical conductivity of the ternary material, while LiFeO$_2$ is expected to improve the stability of the material at the MCFC cathode environment, by lowering the solubility. Further, the chemical potential of each component in the LiFeO$_2$-LiCoO$_2$-NiO ternary materials should be lower than to that in the single candidate materials. Hence, the lower activity decreases the dissolution rate of the ternary materials in the carbonate melt.

The aim of this work was to develop alternative cathode materials for the MCFC in the LiFeO$_2$-LiCoO$_2$-NiO ternary system. A strategical approach of finding alternative materials in the ternary system to replace the existing cathode of the MCFC has been undertaken. It was carried out by investigating the electronic conductivity of the new materials, fabricating porous-gas-diffusion cathodes out of the preferred materials and evaluating their electrochemical performance, during short-time, laboratory-scale cell operation.
2. Experimental Procedure

The experimental work was carried out under three main phases. Synthesis and characterization of powders and sintered materials were done in the first phase. The second phase involved the fabrication of selected materials into porous-gas-diffusion cathodes and characterization of them. The in-cell testing of prepared cathodes and their post cell characterization were performed under the final phase.

2.1. Material preparation and characterization

Synthesis of ceramic powder is a crucial factor in the field of electroceramics. The powder characteristics can affect the subsequent processing steps and influence the properties of the final sintered product. Wet-chemical powder preparation techniques are easy to perform and yield pure fine powder with a good chemical homogeneity. The feasibility of two wet-chemical methods, the glycine-nitrate method and the Pechini method, was investigated in order to obtain powder with characteristics appropriate for MCFC cathode fabrication. For both methods, stoichiometric amounts of metal nitrates were used as starting materials with appropriate organic precursor solutions.

2.1.1. The glycine-nitrate method

![Process flow chart for the Glycine-nitrate process.](image)

The glycine-nitrate method is a rapid and self-sustaining combustion process that is particularly useful for synthesizing very fine, multi-component oxide powders [82-84]. The
process flow chart of the glycine-nitrate method is shown in Figure 2.1. The process undergoes through a direct conversion of the molecular mixture of the precursor solution to the final oxide product, avoiding formation of intermediate crystalline phases that require inter-diffusion for complete reaction. During the self-sustaining combustion, the precursor solution is rapidly converted into an oxide product with glycine serving as the fuel and nitrates providing the oxidant.

2.1.2. The Pechini method
Pechini method, which occurs via an intermediate resin, is based on the ability of certain alpha hydroxy carboxylic acids to form polybasic acid chelates with metallic ions [85-86]. The chelate undergoes polyesterification when heated with a polyalcohol and forms a viscous resin, a glassy polymer and finally the fine oxide powder on further heating. The process flow chart of the Pechini process is shown in Figure 2.2.

![Figure 2.2. Process flow chart for the Pechini process.](image)

2.1.3. Calcination of powder
Both powder synthesis processes were completed by calcining ash products at a higher temperature. The calcination temperature had to be selected considering factors such as particle size and phase purity of calcined powders. However, after some preliminary studies, calcining at 650 °C for two hours in air was chosen as the calcination conditions for the powder batches prepared for material characterization studies.
2.1.4. Characterization of powders

For material characterization studies, small batches (0.2 - 0.3 mole) of powder were prepared. The synthesized powders were characterized for basic powder properties such as specific surface area, density, particle size, particle morphology and phases present. The nitrogen adsorption method (BET, Micromeritics, Gemini 2370) was used for specific surface area measurements and to determine the average particle size (the surface diameter). Density measurement was performed by Pycnometry (Micromeritics, AccuPye 1330). Phase analysis was carried out with X-ray diffraction (XRD, Philips diffractometer using monochromatic Cu Kα radiation) by comparing the obtained patterns with relevant JCPDS (Joint Committee for Powder Diffraction Standards) patterns. Scanning Electron Microscopy (SEM, JEOL JSM-840) was employed to investigate the particle morphology and for further confirmation of particle size determined by BET.

2.1.5. Preparation and characterization of sintered materials

The calcined powders were uni-axially cold pressed at 100 MPa and green pellets of 12 mm in diameter were prepared. The green pellets were subsequently sintered at 1000 °C for two hours in static air. The phases present in the sintered pellets were determined by XRD, and SEM was employed for microstructural analysis.

2.1.6. Electrical conductivity measurements on sintered pellets

The electrical conductivity of these materials was determined by performing d.c. conductivity measurements on sintered pellets by the four-probe method. Before the measurements, the flat end surfaces of pellets were coated with gold paste (G3535, Agar Scientific Ltd., England) or platinum paste (6402 0040/308A, Demetron, Germany) to provide better contact with the electrodes of the measuring probe. The conductivity measurements were performed in a cyclic manner on heating and cooling in air and cathode gas (30% CO2 + 70% air), in the temperature range, 550 - 750 °C.

In order to compare the electrical conductivity of materials measured using pellets with different porosity, the measured conductivity was converted to the specific conductivity (conductivity at theoretical density) using the semi-empirical relationship [87]:

\[
\sigma_s = \sigma (1-P)^{-1.75}
\]  \hspace{1cm} (2.1)

where \(\sigma_s\) is the measured electrical conductivity, \(\sigma\) is the specific electrical conductivity and \(P\) is the porosity.

2.2. Cathode fabrication and characterization

The MCFC cathode design involves a critical pore size distribution, which provides essential micro and macro porosity for a proper cell operation. Most of the MCFC cathode development work with alternative materials involves tape casting of fine ceramic powders. In such circumstances, the appropriate macro porosity is achieved by introducing poreformers into the tape casting process [21, 37, 38]. On the other hand, the essential micro porosity in sintered cathodes is obtained by starting the cathode preparation with fine powder particles. Preferably, the particle size should be in sub-micron size, so that the inter-particle distance of the sintered cathode will be sufficiently small to provide the capillary forces needed for proper electrolyte wetting [21, 38]. Previous work of our research group with LiCoO2 and LiFeO2, has shown that a particle size of about 0.1 - 0.4 \(\mu m\) can result in the appropriate
microporosity in sintered cathodes [37, 38]. Based on the outcome of the material characterization study, the suitable compositions were selected for cathode fabrication. Cathodes were prepared by casting the synthesized powders into green tapes and sintering the green tapes at a high temperature to obtain porous gas diffusion cathodes.

2.2.1. Powder synthesis for cathode preparation
Though grinding can reduce the coarser particles in a later stage, it can cause non-uniform particle size and introduce contaminants to the powder. Therefore, it is more practicable to control the powder particles to the appropriate sub-micron size at the powder synthesis stage. Preliminary calcination studies were performed to find the optimum calcination temperatures, which result in appropriately fine powders. For tape casting, large batches (about 60 g) of powders were prepared by calcining in a pot furnace keeping the powder in alumina crucibles of about 300 ml in volume. When calcining a large powder batch in a crucible like this, the resulting particle sizes from the top and the bottom parts of the powder batch can differ considerably [37]. In order to minimize this effect by enhancing proper mixing of the powder, a stepwise calcination process with intermediate milling was employed in this study.

2.2.2. Tape casting
Nonaqueous slurries containing the cathode material, in the form of sub-micron size powder, with other organic components such as solvent, defloculant, plasticizer and binder were used for tape casting. A poreformer, in the form of plastic spheres of 10 μm in size, was added to the slurry in order to obtain required macro pores in sintered cathodes. Tapes with and without poreformers were prepared in order to study the effect of poreformers on sintered cathodes. Basically, these recipes of tape-casting slurries were identical to those previously developed in our research group for casting LiCoO₂ and LiFeO₂ tapes [21, 37, 38]. However the slurry recipes had to be modified in accordance with the properties of powders used in this study. After an appropriate homogenization and de-airing, the slurry was cast into thin tapes by the doctor blade process using a batch tape-casting unit (CERLIM, Limoge, France).

2.2.3. Cathode sintering
Circular cathodes (22 and 32 mm) cut from the green tapes were sintered in a tube furnace (Lindberg, Type 54479) at high temperatures in static air. Sintering conditions such as temperature, time and environment can influence the properties of sintered cathodes [21, 37, 38]. Specially, the sintering temperature, which can affect the properties of porous cathodes, is a main factor to be considered in optimizing cathodes. Sintering studies to choose the optimum sintering temperatures were carried out by sintering green cathodes at different temperatures ranging from 800 to 1200 °C.

2.2.4. Preliminary characterization of sintered cathodes
The phase analysis of the sintered cathodes was performed by XRD, and SEM was employed for microstructural characterization. Pore size distribution in cathodes was investigated by Mercury porosimetry (Micromeritics, Pore Sizer 9310). The van der Pauw technique [88] was employed to measure the electrical conductivity in air and in cathode gas (30% CO₂ and 70% air), in the temperature range, 600 - 700 °C.

2.3. In-cell testing of prepared cathodes

Based on the performance at the previous cathode fabrication phase, suitable cathodes were selected for electrochemical characterization. The electrochemical performance of cathodes
was studied in a laboratory MCFC unit (ECN, Energieonnderzoek Centrum Netherlands, Petten, The Netherlands) of 3 cm$^2$ area.

2.3.1. The laboratory cell unit
Besides the prepared cathodes, standard components purchased from ECN were used for this study. A eutectic mixture of 62 mole% Li$_2$CO$_3$ and 38 mole% K$_2$CO$_3$ was used as the electrolyte, immobilized in LiAlO$_2$ matrix. The other main components were the Ni(Cr) anode together with stainless steel and nickel current collectors for the cathode and the anode sides, respectively. Gas compositions of 15/30/ 55% O$_2$/CO$_2$/N$_2$ humidified at 30 °C and 80/20% H$_2$/CO$_2$ humidified at 60 °C were used for the cathode and anode respectively. A gold wire immersed in a carbonate melt of the same composition as the electrolyte, and surrounded by 33/67% O$_2$/CO$_2$ gas composition served as the reference electrode. A schematic drawing of the laboratory scale fuel cell is found in the reference [89].

2.3.2. Polarization measurements
The electrochemical performance investigation of cathodes, was based on polarization measurements performed under steady-state conditions, at 650 °C. Polarization measurements were carried out also on the anode and the whole cell, in order to observe the performance of the cell with the prepared cathodes. The cell studies were conducted in order to obtain the cathode performance at the optimal degree of electrolyte filling. It was carried out by starting with a relatively low amount of electrolyte in the cell and then repeatedly adding electrolyte to the cell.

The polarization measurements were carried out with an electrochemical interface (Solartron 1286). The potentials were corrected for the ohmic drop in the cell by employing a current interruption technique. However, this technique may lead to an underestimation of the overpotential for porous electrodes when the electronic conductivity of the electrode is of the same magnitude as the effective ionic conductivity of the pore electrolyte. This underestimation of the overpotential could take place due to the backward currents occurring in the electrodes [43]. Therefore, the resulting potentials were corrected using the formula:

$$\phi = \phi_{\text{ei}} + L \frac{i}{\sigma + \phi}$$  \hspace{1cm} (2.2)

where, $\phi_{\text{ei}}$ is the measured overpotential, $L$ is the thickness of the electrode, $i$ is the current density and, $\phi$ and $\sigma$ are the effective conductivity of the electrode and the electrolyte, respectively.

2.3.3. Post-cell characterisation
After completing the cell test, the fuel cell was cooled down to room temperature and the cathode-current collector assembly was separated from the cell. The assembly was then embedded in epoxy (a mixture of Epofix Resin and Epofix Hardener) and cut, in order to obtain a cross section of the cathode-current collector, by a precision cutting device. The cross section of the cathode-current collector assembly was polished to a mirror finish. The post-cell characterization involved the examination of the cathode-current collector cross section by SEM. The morphology and composition of the corrosion layer formed between cathode and current collector were examined by means of SEM equipped with an Energy Dispersive Spectrometer (EDS).
3. Results and Discussion

This section contains a summary of the outcomes of this work presented in the five appended papers. Furthermore, a brief discussion on the common aspects and trends observed during the study is given with some examples.

3.1. Materials study

Table 3.1. The prepared compositions

<table>
<thead>
<tr>
<th>System</th>
<th>LiFeO$_2$</th>
<th>NiO</th>
<th>LiCoO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Reference materials</td>
<td>-</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>50</td>
<td>-</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>-</td>
<td>50</td>
<td>-</td>
<td>50</td>
</tr>
<tr>
<td>A</td>
<td>94</td>
<td>6</td>
<td>-</td>
</tr>
<tr>
<td>LiFeO$_2$-NiO binary</td>
<td>75</td>
<td>25</td>
<td>-</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>25</td>
<td>75</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>94</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>47.5</td>
<td>47.5</td>
<td>5</td>
</tr>
<tr>
<td>LiFeO$_2$-NiO 1:1</td>
<td>45</td>
<td>45</td>
<td>10</td>
</tr>
<tr>
<td>42.5</td>
<td>42.5</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>40</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>37.5</td>
<td>37.5</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>35</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>71.25</td>
<td>23.75</td>
<td>5</td>
</tr>
<tr>
<td>LiFeO$_2$:NiO 3:1</td>
<td>67.5</td>
<td>22.5</td>
<td>10</td>
</tr>
<tr>
<td>63.75</td>
<td>21.25</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>20.0</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>56.25</td>
<td>18.75</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>52.5</td>
<td>17.5</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>23.75</td>
<td>71.25</td>
<td>5</td>
</tr>
<tr>
<td>LiFeO$_2$:NiO 1:3</td>
<td>22.5</td>
<td>67.5</td>
<td>10</td>
</tr>
<tr>
<td>21.25</td>
<td>63.75</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>20.0</td>
<td>60</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>18.75</td>
<td>56.25</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>17.5</td>
<td>52.5</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>6.67</td>
<td>3.33</td>
<td>90</td>
</tr>
<tr>
<td>LiFeO$_2$:NiO 2:1</td>
<td>13.33</td>
<td>6.67</td>
<td>80</td>
</tr>
<tr>
<td>20</td>
<td>10</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>26.67</td>
<td>13.33</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>33.33</td>
<td>16.67</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>20</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>3.33</td>
<td>6.67</td>
<td>90</td>
</tr>
<tr>
<td>LiFeO$_2$:NiO 1:2</td>
<td>6.67</td>
<td>13.33</td>
<td>80</td>
</tr>
<tr>
<td>10</td>
<td>20</td>
<td>70</td>
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<td>13.33</td>
<td>26.67</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>16.67</td>
<td>33.33</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>40</td>
<td>40</td>
<td></td>
</tr>
</tbody>
</table>

The compositional details of the materials prepared in this study are given in Table 3.1 and the mole percentages given in the table are for the nominal compositions. The binary
compositions are mainly from the LiFeO$_2$-NiO binary system, however, few compositions in the LiCoO$_2$-LiFeO$_2$ and LiCoO$_2$-NiO binary systems were also prepared at the beginning of this work. System A consists of the LiFeO$_2$-NiO binary compositions, while System R contains some other binary materials together with LiFeO$_2$, LiCoO$_2$ and NiO, prepared for reference purposes. Each of the B to F ternary sub-systems consists of the LiFeO$_2$-LiCoO$_2$-NiO ternary materials with a constant molar ratio of LiFeO$_2$:NiO and varying LiCoO$_2$ contents. The corresponding LiFeO$_2$:NiO molar ratios for the systems B, C, D, E and F are 1:1, 3:1, 1:3, 2:1 and 1:2, respectively.

The materials prepared in B, C and D systems are based on the ternary compositions starting from the LiFeO$_2$-NiO binary system and extending towards the LiCoO$_2$ end of the ternary system. Ternary compositions of up to 30 mole% of LiCoO$_2$ were studied under each of the B, C and D systems. These ternary compositions, which are rich in LiFeO$_2$ and NiO, are referred here as the LiFeO$_2$-NiO rich compositions. On the other hand, LiCoO$_2$ rich ternary compositions were studied under systems E and F. Ternary compositions starting from the LiCoO$_2$ end and extending down to 40 mole% LiCoO$_2$ were studied under these systems.

### 3.1.1. Feasibility of powder preparation methods

Initially, the work was limited to a few selected binary and ternary compositions. These powder compositions were synthesized by the glycine-nitrate method, following a procedure similar to that of Bloom et al. [78], by calcining at 550 °C for four hours in static air. Thereafter, these powders were pelletized and pellets sintered at 1000 °C were subjected to d.c electrical conductivity measurements. The powders prepared by the glycine-nitrate process are around 0.1 - 0.2 mm in size and contain irregular shaped particles of a sponge or porous powder structure (see Figure 1 and 2 in Paper IV). The BET and electrical conductivity data obtained on these materials prepared by the glycine-nitrate process is given in Table 3.2.

### Table 3.2. Details of the materials prepared by the glycine-nitrate process.

<table>
<thead>
<tr>
<th>Composition (mole%)</th>
<th>Specific Surface area (m$^2$/g)</th>
<th>Particle size (μm)</th>
<th>Conductivity at 650 °C in cathode gas (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>In air</td>
</tr>
<tr>
<td>LiFeO$_2$</td>
<td>NiO</td>
<td>LiCoO$_2$</td>
<td>8.1</td>
</tr>
<tr>
<td>94.0</td>
<td>6.0</td>
<td>0.0</td>
<td>7.5</td>
</tr>
<tr>
<td>50.0</td>
<td>50.0</td>
<td>0.0</td>
<td>6.5</td>
</tr>
<tr>
<td>12.5</td>
<td>87.5</td>
<td>0.0</td>
<td>5.3</td>
</tr>
<tr>
<td>10.0</td>
<td>90.0</td>
<td>0.0</td>
<td>4.6</td>
</tr>
<tr>
<td>6.0</td>
<td>94.0</td>
<td>0.0</td>
<td>8.8</td>
</tr>
<tr>
<td>40</td>
<td>20</td>
<td>40</td>
<td>10.2</td>
</tr>
</tbody>
</table>

Considering the electrical conductivity of these materials, 10 mole% LiFeO$_2$ - 90 mole% NiO binary composition (of System A) and 40 mole% LiFeO$_2$ - 40 mole% NiO - 20 mole% LiCoO$_2$ ternary composition (of System B) were selected for cathode preparation via tape casting. However, preparation of cathodes free of cracks and with even thickness, from the powders prepared by the glycine-nitrate method, was very difficult. Since cathodes were ex-situ sintered in the present study, the problems associated with cathodes prepared from powder synthesized by the glycine-nitrate method could easily be detected.

Most of these difficulties might be resulted from improper particle properties associated with the sponge or porous structure of the powders prepared by the glycine-nitrate method. In
contrast, powders of the same compositions prepared by the Pechini method show rather spherical shaped, less porous and less irregular sub-micron size particles (see Figure 1 and 2 in Paper IV). Though these powders are coarser and the electrical conductivity of the materials synthesized by them is slightly lower, the cathode preparation with powder, synthesized by the Pechini method was much easier and successful. Therefore all the remaining powder compositions for this study were synthesized by the Pechini method.

The work on the LiFeO$_2$-NiO binary compositions of System A was first performed and based on its outcome the study was thereafter extended to the LiFeO$_2$-NiO rich ternary compositions of systems B, C and D. Among these ternary sub-systems, System B was first investigated. Thereafter, based on the out come of System B, the work on systems C and D was simultaneously carried out. Later, the studies on LiCoO$_2$ rich ternary compositions were carried out, performing the work simultaneously on system E and F.

3.1.2. Phase analysis of sintered materials

The phase details of the prepared materials are shown in Figure 3.1. The compositions, given in the figure, are in mole percentages and the phase details are based on the XRD analysis.
performed on pellets sintered at 1000 °C for two hours in static air. The phase analysis by XRD, indicated the existence of LiFeO$_2$-NiO rich solid solutions, of the $Fm\overline{3}m$ cubic rock-salt structure, in the LiFeO$_2$-NiO binary materials prepared under System A. This behavior for the materials prepared by the Pechini method in this study is identical to that reported by Bloom et al. with their materials prepared by the glycine nitrate method or mixed-oxide route [78].

As seen in Figure 3.1, the ternary materials of systems B, C and D, containing low LiCoO$_2$ contents, form solid solutions of the $Fm\overline{3}m$ cubic rock-salt structure rich in LiFeO$_2$ and NiO. The boundary between the LiFeO$_2$-NiO rich solid solution and the multiphase zone is slightly varying among the B, C and D ternary sub-systems (see Figure 4 in Paper I and, Figure 2 and 3 in Paper II). The apparent solid solution boundary is in between 10 and 15 mole% of LiCoO$_2$ for System B and C while it is slightly high, in between 15 and 20 mole% of LiCoO$_2$, for System D. Hence, this XRD phase analysis of the present study indicates a slightly lower level for the LiFeO$_2$-NiO rich solid solution boundary than suggested by Bloom et al. [78]. According to the simple linear extrapolation of their experimental data, the solid solution region is extending from the LiFeO$_2$-NiO line out to about 18 mole% LiCoO$_2$. This deviation might be due to the differences in materials synthesis in both studies.

In LiCoO$_2$ rich materials prepared under the systems E and F, the content of the LiFeO$_2$-NiO rich solid solution phase, decreases with increasing LiCoO$_2$ content in the composition (see Figure 2 and 3 of Paper III). Instead, the content of LiCoO$_2$-rich phase increases at the expense of the LiFeO$_2$-NiO rich solid solution phase. Based on simple linear extrapolation of their experimental data, Bloom et al. suggested the formation of a solid solution region (of the $R3m$ layered rock salt structure), extending to 12 mole% LiFeO$_2$ and 5 mole% NiO from the LiCoO$_2$ end material [6, 77, 78]. Similarly, the phase analysis of the present study indicates the possibility of the formation of LiCoO$_2$-rich LiFeO$_2$-LiCoO$_2$-NiO solid solution region close to the LiCoO$_2$ end of the ternary system.

### 3.1.3. Electrical conductivity of prepared materials

The d.c. electrical conductivity measurements were performed by the four probe method, during heating and cooling in a cyclic manner, in the temperature range, 550 - 750 °C. It was observed in these measurements that the first measuring cycle yields the highest conductivity while succeeding cycles show lower conductivity. However, the conductivity becomes almost stable after few heating cycles (see Figure 7 of Paper IV). The considerably large decay in conductivity during the first few cycles may be due to altering the defect structure of the as-sintered specimen to more stable defect structure. Thus, it indicates some dependence of electrical conductivity on heating profiles of the measuring procedure. Hence care should be taken when presenting electrical conductivity data out of such measurements.

Throughout the measured temperature range, the electrical conductivity of these materials increases in an exponential manner with temperature, as could be expected for semiconductors. However, the trend of increasing conductivity with temperature is different among the materials (see Figure 2 and 5 in Paper I, Figure 4 and 5 in Paper II, and Figure 4 and 5 in Paper III). The variation of the specific electrical conductivity of LiFeO$_2$-NiO binary compositions with LiFeO$_2$ content, at 650 °C in cathode gas, is shown in Figure 3.2. (also see Table I in Paper I). As expected, the electrical conductivity of these binary compositions decreases with increasing LiFeO$_2$ content and it can be ascribed to the very low electrical conductivity of LiFeO$_2$ with compared to NiO [26].
To minimize the dissolution of MCFC cathode, it is desired to have highest possible LiFeO$_2$ content in the material [77]. On the other hand, materials for MCFC cathode application are generally required to possess a minimum electrical conductivity of 1 S/cm to facilitate a proper electrical conduction in the cathode at the working conditions [6, 33, 34]. As shown in Figure 3.2, the 10 mole% LiFeO$_2$-90 mole% NiO binary composition of System A, possesses an electrical conductivity of about 1 S/cm at 650 °C in cathode gas. Subsequently, the conductivity decreases rapidly with the increase of LiFeO$_2$ content. By considering both these factors, the 10 mole% LiFeO$_2$ composition was selected for cathode preparation from LiFeO$_2$-NiO binary system.

![Figure 3.2](image-url)

*Figure 3.2. The variation of the specific electrical conductivity of LiFeO$_2$-NiO binary materials with LiFeO$_2$ content, at 650 °C in cathode gas (30% CO$_2$ + 70% air).*

A considerably different electrical conductivity behavior was noticed in the ternary materials and the variation of the specific electrical conductivity of them with LiCoO$_2$ content, at 650 °C in cathode gas, is shown in Figure 3.3. (also see Table III in Paper I, Table I and II in Paper II, and Table I and II in Paper III). A similar trend of increasing conductivity with the content of LiCoO$_2$ in the material, can be noticed in the LiFeO$_2$-NiO rich ternary compositions prepared under systems B, C and D.

In each of systems B, C, and D, the increase of LiCoO$_2$ content of the material increases the conductivity to a maximum, followed by a decrease in conductivity with further increasing of LiCoO$_2$ content. This conductivity maximum is slightly shifting towards the materials with higher LiCoO$_2$ content, with decreasing the LiFeO$_2$: NiO ratio in the system. The maximum is shifting from about 20 to 25 mole% of LiCoO$_2$ content, when the LiFeO$_2$: NiO ratio is changing from 3:1 (System C) to 1:3 (System D).

As shown in Figure 3.3, when comparing the electrical conductivity among these LiFeO$_2$-NiO rich ternary materials (System B, C and D) with the same LiCoO$_2$ content, the materials in
System D (with the lowest LiFeO\textsubscript{2}:NiO molar ratio, 1:3) show the highest conductivity. The materials in System C (with the highest LiFeO\textsubscript{2}:NiO molar ratio, 3:1) show the lowest conductivity, while the conductivity of materials in System B lies in between. This behavior is identical to that of the LiFeO\textsubscript{2}-NiO binary system; the electrical conductivity decreases with increasing LiFeO\textsubscript{2} content in the material, due to very low electrical conductivity of LiFeO\textsubscript{2}.

![Graph showing electrical conductivity vs LiCoO\textsubscript{2} mole%](image)

*Figure 3.3. The variation of the specific electrical conductivity of ternary compositions with LiCoO\textsubscript{2} content, at 650 °C in cathode gas (30% CO\textsubscript{2} + 70% air).*

The electrical conductivity behavior of the LiCoO\textsubscript{2} rich ternary materials prepared under systems E and F is also presented in Figure 3.3. A slightly different behavior, in the variation of conductivity with LiCoO\textsubscript{2} content, can be seen in these two systems. In System E, the conductivity increases to a maximum at around 50 mole% with decreasing LiCoO\textsubscript{2} content, followed by a decrease in conductivity with further decreasing of LiCoO\textsubscript{2} content down to 40 mole%. In System F, the conductivity increases continuously with decreasing LiCoO\textsubscript{2} content of the composition down to 40 mole%.

Due to the low electrical conductivity of the prepared materials, it was not intended to continue the study in System C. On the other hand, the electrical conductivity results raised some hopes on the materials, especially in systems B and D, as promising candidates for MCFC cathode application. Besides the electrical conductivity, there were some other interesting factors, such as the differences between single-phase and multiphase materials, to be considered. Single-phase materials are believed to be more preferable for MCFC cathode application since they are considered as more stable in the working environment. By considering that, the ternary materials, 10 mole% LiCoO\textsubscript{2} of System B and 15 mole% LiCoO\textsubscript{2} of System D, which show the highest conductivity among the single-phase materials of respective system, were selected for cathode fabrication. However, as presented later in this thesis (see section 3.3.2.), the electrochemical performance of cathodes prepared from single-phase materials was extremely poor.
As mentioned in section 1.4., so far, none of the earlier proposed alternative single-phase materials could satisfactorily substitute the lithiated NiO. As a result, much interest has recently been directed towards non single-phase materials such as multiphase materials and coatings [59, 70, 71]. The materials, which show the highest electrical conductivity in each of the ternary system in this study, are multiphase materials. Though they are multiphase materials, they contain LiFeO$_2$-NiO rich and LiCoO$_2$ rich LiFeO$_2$-LiCoO$_2$-NiO solid solution phases, all of which are regarded possessing desirable characteristics for MCFC cathode application. By considering these factors, the multiphase materials, which show promising electrical conductivity in each of System B, D, E and F, were also selected for further studies through cathode preparation.
3.2. Cathode fabrication study

In order to achieve the desired performance, the MCFC cathode should possess an appropriate pore structure with porosity, 50 - 80%, and a dual pore size distribution comprised of essential macro (> 1 μm) and micro (< 1 μm) porosity [5, 6]. To obtain the appropriate micro porosity as well as high effective surface area for chemical reactions, it is always useful to start the cathode preparation with fine powders containing sub-micron size particles.

Table 3.3. Details of materials selected for cathode preparation

<table>
<thead>
<tr>
<th>System</th>
<th>Composition (mole%)</th>
<th>Powders for tape casting</th>
<th>Specific conductivity at 650 °C (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LiFeO₂</td>
<td>NiO</td>
<td>LiCoO₂</td>
</tr>
<tr>
<td>A</td>
<td>10</td>
<td>90</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>45</td>
<td>45</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>40</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>37.5</td>
<td>37.5</td>
<td>25</td>
</tr>
<tr>
<td>D</td>
<td>21.25</td>
<td>63.75</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>60</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>18.75</td>
<td>56.25</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>17.5</td>
<td>52.5</td>
<td>30</td>
</tr>
<tr>
<td>E</td>
<td>33.33</td>
<td>16.67</td>
<td>50</td>
</tr>
<tr>
<td>F</td>
<td>20</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>R</td>
<td>-</td>
<td>100</td>
<td>-</td>
</tr>
</tbody>
</table>

3.2.1. Powder for cathode preparation

The details of the materials selected for cathode preparation are given in Table 3.3. The preliminary calcination studies performed on these powder compositions showed the increasing of particle size with the calcination temperature throughout the studied temperature range, 500 - 750 °C (see Figure 3 in Paper I(c)). Thus, a lower calcination temperature is desired in order to obtain finer powder with higher specific surface area. However, the powder calcined at temperatures lower than 550 °C showed the existence of considerable amounts of residual phases, which obstructed selecting a calcination temperature lower than 550 °C.

Large batches (about 60 g) of powder for cathode preparation were calcined at selected temperatures by employing step-wise calcination processes with intermediate milling. As seen in Table 3.3, even after sintering at 550 °C the compositions with high NiO contents possess relatively larger powder particles. However, most of the other ternary powders gave considerably smaller particles of around 0.3 μm, even after sintering at temperatures above 550 °C.

3.2.2. Porous gas diffusion cathodes

Some of the different optimized slurry recipes used for tape casting in this study are given in Table II in Paper V. The difference between the content of the slurry constituents in these recipes are mainly due to the differences of the powder densities, hence the difference in specific volume of the powders. However, other properties such as specific surface area,
hence the particle size, and size distribution of powder may also affect the contents of the slurry constituents in the optimized recipe.

The effect of introducing poreformers as well as the poreformer content on the properties of sintered cathodes were investigated by preparing cathodes without poreformers and with different content of poreformer. In addition, comprehensive sintering studies to choose the optimum sintering temperatures were carried out with each of the green tapes, by sintering cathodes at different temperatures ranging from 800 to 1200 °C. A brief description of the outcome of the cathode fabrication study is given in the following sections (3.2.3 to 3.2.5).

These porous sintered cathodes should possess a sufficient mechanical strength to be handled in the cell assembling. In general, cathodes sintered at higher temperatures show better mechanical strength. Therefore the mechanical strength of sintered cathodes is also a very important factor to be considered when selecting an optimum sintering temperature. The lowest sintering temperature for these sintering studies was determined by this strength factor.

3.2.3. Phases present in sintered cathodes
The XRD phase analysis shows the formation of Fe₂O₃ and Co₃O₄ additional phases in cathodes sintered at higher temperatures due to possible evaporation of Li from the cathode material. The 10 mole% LiFeO₂ cathodes of System A sintered at temperatures up to 1100 °C showed the presence of only the LiFeO₂-NiO solid-solution phase. However, an additional Fe₂O₃ phase was detected in cathodes sintered at 1200 °C (see Figure 1 in Paper V), although no evidence for the existence of such Fe₂O₃ secondary phase could be found in dense pellets sintered at 1200 °C.

Moreover, formation of an extra Co₃O₄ phase in cathodes sintered at higher temperatures could be observed in cathodes prepared from materials containing LiCoO₂. An example for this behavior is given in Figure 2 of Paper V with the cathodes prepared from 20 mole% LiCoO₂ composition of System D. The cathodes sintered at low temperatures show the presence of only the phases detected in respective cathode material (in the form of dense pellets). In addition, a minor phase of Co₃O₄ could be detected in porous cathodes sintered at higher temperatures, though no such secondary phase could be detected in dense pellets sintered at the same temperature.

In comparison to dense pellets, the higher surface area of thin porous cathodes may facilitate for more Li evaporation from LiFeO₂ and LiCoO₂, causing traces of Fe₂O₃ and Co₃O₄ phases, respectively, in cathodes sintered at higher temperatures. This kind of Li evaporation and Co₃O₄ formation was observed in this study for cathodes prepared with LiCoO₂-rich ternary compositions by sintering at higher temperatures. However, the temperature, at which Li evaporation and Co₃O₄ formation begin, varies among the materials. Since these newly formed Fe₂O₃ and Co₃O₄ phases may degrade the performance of the MCFC cathode, it was not intended to sinter cathodes at such high temperatures. Hence, the upper temperature limit for the cathode sintering studies was determined by this phase purity factor.

3.2.4. Pore structure of cathodes
Introduction of poreformers into the cathode preparation process significantly changes the pore structure of sintered cathodes. An example showing the effect of introducing poreformers in the cathode preparation process is given in Figure 3.4. (see also Figure 3 and Table II of Paper I). The cathodes prepared without poreformers show a narrow pore size distribution with rather fine pores and relatively low total porosity. An appropriate pore
structure containing sufficient micro (< 1 µm) and macro (> 1 µm) pores with significantly increased total porosity could be achieved in cathodes prepared with poreformers and fine powders. This type of bimodal pore structure, which is comparable to that of lithiated NiO, is a basic requirement for proper operation of the MCFC cathode [5].

![Figure 3.4. The porosimetry data of 10 mole% LiFeO₂ cathodes prepared with and without (*) poreformers and sintered at different temperatures.](image)

Figure 3.4. The porosimetry data of 10 mole% LiFeO₂ cathodes prepared with and without (*) poreformers and sintered at different temperatures.

![Figure 3.5. SEM micrograph showing a 25 mole% LiCoO₂ cathode of System B, prepared with poreformers and sintered at 1000 °C for two hours. The specimen was vacuum infiltrated with plastic resin.](image)

Figure 3.5. SEM micrograph showing a 25 mole% LiCoO₂ cathode of System B, prepared with poreformers and sintered at 1000 °C for two hours. The specimen was vacuum infiltrated with plastic resin.
The SEM micrograph shown in Figure 3.5 gives further evidence for the existence of such bimodal pore structure with the appropriate micro and macro pores. The cathodes prepared with different material compositions using sub-micron size powder particles and plastic poreformers, in this study, showed quite a similar pore structure with an appropriate bimodal pore size distribution. However the porosity, the average pore size as well as the peak positions of the bimodal pore size distribution are slightly different for the different cathode.

The amount of poreformers added to the tape casting slurry considerably affect the properties of sintered cathodes (see Figure 6 and Table III in Paper III, and Figure 6 and Table III in Paper V) When decreasing the poreformer content, the total porosity together with macro porosity of the cathode decreases and the peak position of the macro porosity shifts towards finer pores. However, decreasing of poreformer content considerably increases the effective electrical conductivity of the porous cathodes. Accordingly, it indicates the nature of the compromise to be made between electrical conductivity and pore structure, in optimizing the tape casting slurry in order to prepare the best cathodes out of a given powder composition. Quite a similar behavior was noted with other powder compositions used for cathode preparation in this study. However, the effect of poreformer content on the pore structure and the electrical conductivity of sintered cathodes slightly varied, depending on the properties of the powders and slurry recipes used for cathode preparation.

The effect of sintering temperature on the pore structure of cathodes is illustrated in Figure 3.4. with 10 mole% LiFeO₂ cathodes of System A prepared with poreformers. (also see Table II in Paper I). In general, it was observed in this study that the increase of sintering temperature shifts the macro porosity towards finer pores and also decrease the total porosity together with the macro and micro porosity. This behavior can be ascribed to more densification, hence reducing porosity in the cathode, when increasing the sintering temperature. Hence, the cathodes sintered at low temperatures show a more appropriate pore structure, with larger macro pores and higher total porosity, than that of cathodes sintered at high temperatures.

3.2.5. Electrical conductivity of cathodes
The electrical conductivity of sintered cathodes was measured by the van der Pauw method, in the temperature range between 600 and 700 °C, first in air and then in cathode gas (30% CO₂ + 70% air). The electrical conductivity of all the studied cathodes increases with temperature, in both air and cathode gas, throughout the studied temperature range, suggesting semi-conducting nature for the cathode material. An example for this typical conductivity behavior of sintered cathodes is given in Figure 3.6.

The electrical conductivity behavior of cathodes prepared with 20 mole % LiCoO₂ of System D by sintering at 900, 950 and 1000 °C, in cathode gas (30% CO₂ + 70% air), is shown in the figure. All the cathodes prepared in this study, with different materials and by sintering at different temperatures, show a similar behavior in both air and cathode gas. However, the trend of increasing conductivity varies between the different cathodes and it may largely be due to factors such as specific conductivity of the cathode material, sintering temperature and porosity of the cathode.

As expected, the measured electrical conductivity of the cathodes prepared without poreformers is relatively higher than that of the cathodes prepared with poreformers. Among
the cathodes prepared with poreformers, the measured conductivity increases, both in air and in cathode gas, with increasing sintering temperature (see Table II and IV in Paper I, Table III in Paper II, Table III and IV in Paper III, Table III in Paper V). Thus the conductivity results propose sintering cathodes at higher temperatures, in order to obtain cathodes with higher electrical conductivity. The increase in measured conductivity in cathodes prepared with less poreformers or sintered at higher temperatures, can be ascribed to reduced porosity, hence better connectivity between particles in the cathode.

![Figure 3.6. Variation of the measured electrical conductivity in cathode gas (30% CO₂ + 70% air), of 20 mole% LiCoO₂ cathodes of System D sintered at 900, 950 and 1000 °C.](image)

**3.2.6. Selection of cathodes for cell testing**

These cathode sintering studies point out the main factors to be considered when selecting an optimum sintering temperature. When considering the electrical conductivity of the cathode, a higher sintering temperature is desired to obtain cathodes with higher electrical conductivity. A higher sintering temperature is also desired to improve mechanical strength of porous cathodes. However, according to porosimetry study, higher sintering temperatures degrade the porestructure. Also as mentioned in section 3.2.3, the cathodes sintered at higher temperatures contain undesirable additional phases. Thus the optimum sintering temperatures were chosen making compromises among these main factors, for each individual case of prepared tapes.

Thin porous cathodes of 0.2 - 0.4 mm in thickness, with sufficient mechanical strength for cell testing, could be obtained by sintering at the selected temperatures. As mentioned in section 3.3.4., all these sintered cathodes show promising pore structure for MCFC cathode operation. Further, the total porosity of most of these cathodes could be confined to the range, 55 - 65%. The details of the cathodes sintered at the respective optimum temperatures are given in Table 3.4. The specific electrical conductivity of the corresponding cathode material (based on the conductivity performed on sintered pellets) is given within parenthesis under the last column of the table.
As seen in Table 3.4, the measured effective electrical conductivity varies in a wide range, 0.027 - 0.86 S/cm. This variation may to some extent be related to the differences in powder properties of the starting materials and the cathode fabrication process. In particular, the specific electrical conductivity of the cathode material may, to a large extent, influence the effective electrical conductivity of the final cathode. In general, the materials with higher specific electrical conductivity result in higher effective conductivity in porous cathodes. However, the resulting effective conductivity in porous cathodes prepared in this study, is always considerably lower than that expected from the specific electrical conductivity of materials used for cathode fabrication (see Table 3.4).

As given in Table 3.4, the estimated specific electrical conductivity (using Equation 2.1) for these cathodes varies between 0.1 and 3.41. The NiO reference cathode prepared in this study shows an estimated specific electrical conductivity of 1.9 S/cm. Fontes et al [89] suggested a specific conductivity of 0.8 S/cm to be sufficient for making high performance MCFC cathodes. In light of this, all these cathodes, except 10 mole% LiFeO₂ cathode of System A and 10 mole% LiCoO₂ cathode of System B, possess adequate electrical conductivity for MCFC application.

As seen in Table 3.4., the specific electrical conductivity estimated for porous cathodes is considerably lower than that of the material used for cathode fabrication. Moreover, the cathode materials with low specific electrical conductivity (1 - 3 S/cm) result in extremely poor effective conductivity as well as low specific conductivity in porous cathodes. This unexpectedly low conductivity may be resulted in due to the influence of factors such as microstructure, porosity, present phases and phase purity of the cathode. Hence, though 1 S/cm of specific electrical conductivity is generally believed to be adequate for a MCFC cathode material [26], this study suggests to select LiFeO₂-LiCoO₂-NiO materials with higher specific electric conductivity for cathode fabrication.
3.3. Electrochemical performance study

In-cell testing of some selected cathodes was performed in order to study the electrochemical performance of the prepared cathodes at the optimal degree of electrolyte filling. In each case, the cell was started with relatively low electrolyte amount and the electrolyte was repeatedly added to the cell.

3.3.1. Common trends observed in cell studies

Figure 3.7. The cell performance with 25 mole% LiCoO$_2$ cathode of System D. Each triangular marker in the figure represents an addition of about 15 mg of carbonate to the cell.

All cell tested cathodes showed quite a similar behavior with respect to time and added carbonate amount. An example for this typical behavior is given in Figure 3.7. (see also Figure 8 in Paper I and Figure 8 in Paper II). The measured potentials, at a current density of 160 mAcm$^{-2}$, as a function of time are shown in Figure 3.7. The measured iR-corrected cathode potentials were corrected for backward currents using Equation 2.2. The performance of this 25 mole% LiCoO$_2$ cathode of System D, as a function of the amount of carbonate added to the cell, is shown in Figure 3.8. (see Figure 9 in Paper I for 25 mole% LiCoO$_2$ cathode of System B). The iR-corrected polarization curves obtained on this cathode at different levels of carbonate additions are given in Figure 3.9.

The notations in Figure 3.9 correspond to the amount of carbonate added to the cell given in Figure 3.8. The slope of the linear region of the polarization curve at low current densities corresponds to the total polarization resistance. From a to c, it indicates the lowering of polarization resistance with the added amount of the electrolyte. However, the resistance
again increases with further addition of electrolyte from c to e. The upward bending indicates increasing mass-transfer resistance with increasing current density.

**Figure 3.8.** Performance of 25 mole% LiCoO$_2$ cathode of System D, as a function of the amount of carbonate added to the cell

**Figure 3.9.** iR-corrected polarization curves obtained for 25 mole% LiCoO$_2$ cathode of System D, at different levels of carbonate addition.
In general, the polarization of the cell and the cathode decrease with electrolyte addition to an optimum level followed by increase of them with further addition of the electrolyte, in all the cell studies. Therefore this study suggests an optimum level of electrolyte filling in the cell components to achieve the best performance. However, this analysis is based on the amount of electrolyte added to the cell and not on the degree of electrolyte filling in the cell components.

Further, the iR drop of the cell and the cathode decrease continuously with the time and the addition of the electrolyte. The anode polarization was almost constant throughout the study. A similar behavior of the cell and the electrodes was observed with other cell tests carried out with the prepared cathodes in this study. However, the performance of the cathodes, hence the cells, was drastically varying with different cathodes.

3.3.2. Electrochemical performance of cathodes

Initially, cathodes prepared from two single-phase materials (10 mole% LiFeO\textsubscript{2} cathode of System A and 10 mole% LiCoO\textsubscript{2} cathode of System B) were subjected to electrochemical performance studies in the cell. The cell performance of both cathodes was extremely poor, showing exceptionally high cathode polarization and iR-drop in the cathode side. Even at the optimum conditions, both the iR-corrected cathode polarization and the iR-drop at the cathode were some hundreds of millivolts at the current density of 160 mA cm\textsuperscript{-2}.

The cumulative pore volume data of the cathodes used for cell testing is shown in Figure 3.10. Even though these tested cathodes showed quite a favorable pore structure, the very poor effective electrical conductivity of the porous cathode (see Table 3.4) might cause the adverse performance. As mentioned in Section 3.2.6, despite the cathode materials possess higher...
specific electrical conductivity than 1 S/cm, the effective conductivity of the porous cathodes was extremely low (about 0.03 S/cm). Accordingly, these results suggest the use of cathodes prepared from materials with higher electrical conductivity. However, it was not intended to study the LiFeO$_2$-NiO binary compositions containing more NiO than the cell tested material of 10 mole% LiFeO$_2$-90 mole% NiO.

Table 3.5. Details of the electrochemical performance of cell tested cathodes, obtained at the optimum conditions of the respective cell studies.

<table>
<thead>
<tr>
<th>System</th>
<th>B</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition in mole%</td>
<td>LiFeO$_2$</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>NiO</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>LiCoO$_2$</td>
<td>10</td>
</tr>
<tr>
<td>Cathode performance at the optimum condition</td>
<td>IR-corrected polarization (mV)</td>
<td>216</td>
</tr>
<tr>
<td></td>
<td>Cathodic IR-drop (mV)</td>
<td>367</td>
</tr>
</tbody>
</table>

Among the ternary materials, the materials, which possess the highest electrical conductivity in the LiFeO$_2$-LiCoO$_2$-NiO ternary system, are multiphase materials. Considering mainly the electrical conductivity, the cathodes showing the highest effective conductivity in System B and D were selected for cell testing (see Table 3.4). The details of the electrochemical performance of these cell tested cathodes, obtained at optimum conditions of respective cell, are given in Table 3.5. The iR corrected cathode polarization curves of these cathodes, obtained at optimum conditions of respective cell studies, are given in Figure 3.11.

Figure 3.11. The iR corrected cathode polarization curves, obtained at the optimum conditions of respective cell studies.

Compared to previous cell tested cathodes, the performance of the 25 mole% LiCoO$_2$ cathode of System B is much better, with an acceptably low cathode polarization. Though the cathodic iR-drop of this cathode is considerably high, the cathode polarization is close to that reported.
for LiCoO₂ cathodes [21, 38]. When considering the composition of this cathode the obtained performance especially with a considerably high content of LiFeO₂ (37.5 mole%) is particularly interesting (see Table 3.5). The high cathodic iR-drop of this cathode may result from low effective electrical conductivity of the porous cathode (see Table 3.4). In addition, bad contacts between the cathode and its current collector as well as poor electrical conductivity of the corrosion layer formed between them (see section 3.3.3), may also contribute to the high iR-drop.

The 20 and 25 mole% LiCoO₂ cathodes, which show promising effective electrical conductivity, were selected for cell testing from System D. Both cathodes show better performance than previously studied cathodes, with considerably low cathode polarization and iR-drop (see Table 3.5). Among them, the performance of the 20 mole% LiCoO₂ cathode is more preferred, with a suitably low cathode polarization and very low cathodic iR-drop. The performance of this cathode is interesting and far better than other studied LiFeO₂-LiCoO₂-NiO cathodes prepared in this study. The cathodic iR-drop is far lower, while the polarization is in the same order with those reported for LiCoO₂ cathodes [21, 38]. This result suggests the existence of a very low contact resistance between the cathode and the current collector compared to that of LiCoO₂ cathodes. Further, the performance of this cathode is almost comparable to that expected for the NiO cathode in a commercial fuel cell [8].

A comparison between the cell performance of the 20 and 25 mole % LiCoO₂ cathodes of System D, points out some important factors to be considered in order to improve these cathodes. As given in Table 3.4, the effective electrical conductivity of the 25 mole% LiCoO₂ cathode is considerably higher than that of the 20 mole% LiCoO₂ cathode. However, according to the porosimetry results, (Table 3.4 and Figure 3.10) a significant difference in pore structure is seen in these cathodes. The 20 mole % LiCoO₂ cathode show a more favorable pore structure with a higher total porosity (64.3 %), while 25 mole% LiCoO₂ cathode had a lower porosity (52.1%) with less macro pores. Despite its higher electrical conductivity, the improper pore structure of the 25 mole% LiCoO₂ cathode could cause the low performance.
3.3.3. Post-cell characterization of cathodes

The post-cell characterization involved the examination of the cross section of cathode-current collector assembly by SEM. Figure 3.12 shows a SEM micrograph of the cell tested 25 mole% LiCoO$_2$ cathode of System B with electrolyte, after running about 1000 hours in the lab-cell. The carbonate electrolyte is clearly seen in this micrograph obtained on the cathode tested with repeated addition of the electrolyte. Further, the micrograph gives the evidence for existence of an electrolyte film on the agglomerate surface. However, it is difficult to know if the carbonate distribution shown in the micrograph is the same as when the cell was under operation.

![SEM micrograph of the cell tested 25 mole% LiCoO$_2$ cathode of System B with electrolyte, after running about 1000 hours in the lab-cell.](image)

The cross section of 25 mole% LiCoO$_2$ cathode of System B and AISI 310 current collector assembly, after running 1000 hours in the lab-cell is shown in Figure 3.13. In this specimen prepared for SEM study, the cathode material was not in good contact with the current collector. However, it is difficult to say whether it lost the contact in specimen preparation, in cell cooling or even before, during operation.

As seen in Figure 3.13, a corrosion layer of around 15-20 μm in thickness has been formed between the cathode and the current collector. The chemical composition of the corrosion layer was analyzed by SEM equipped with an Energy Dispersive Spectrometer (EDS). The compositions in several points close to cathode-current collector interface are given in Table 3.13. Due to its low atomic weight, Li can not be detected by EDS. However, the presence of lithium ions in the carbonate melt promotes the formation of lithium containing oxides. The base material of the AISI 310 current collector is given at point A. Moving towards the cathode, a chromium depleted layer is found (point B). It arises due to the fact that chromium is more readily oxidized than the other present metal elements.
A chromium-rich layer (point C) is seen followed by a porous iron-rich layer (point D). The boundary between the chromium-rich and the iron-rich layers is clearly seen due to the presence of a continuous crack. The crack might be formed during cell cooling, caused by possible differences in thermal expansion coefficients of adjacent chromium-rich and iron-rich layers. This iron-rich layer could contain iron oxides with dissolved Ni and small amounts of Cr and Co.

Table 3.6. Compositions in the interface between the cathode (37.5 mole% NiO + 37.5 mole% LiFeO$_2$ + 25.0 mole% LiCoO$_2$) and AISI 310 current collector. The compositions are given in weight percentages.

<table>
<thead>
<tr>
<th>Point</th>
<th>O</th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-</td>
<td>24.3</td>
<td>54.8</td>
<td>20.9</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>-</td>
<td>12.3</td>
<td>55.7</td>
<td>32.0</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>3.1</td>
<td>71.8</td>
<td>19.1</td>
<td>6.0</td>
<td>-</td>
</tr>
<tr>
<td>D</td>
<td>1.5</td>
<td>-</td>
<td>84.4</td>
<td>15.1</td>
<td>-</td>
</tr>
<tr>
<td>E</td>
<td>28.5</td>
<td>-</td>
<td>61.2</td>
<td>7.4</td>
<td>2.6</td>
</tr>
<tr>
<td>F</td>
<td>31.1</td>
<td>-</td>
<td>46.1</td>
<td>15.2</td>
<td>7.6</td>
</tr>
</tbody>
</table>

The cross section of the cathode-current collector assembly of 25 mole% LiCoO$_2$ cathode of System D, after running about 1200 hours in the lab-cell, is shown in Figure 3.14. The formation of a corrosion layer of around 10-15 μm in thickness is seen in the figure. Further, this corrosion layer seems to be less porous than that with above mentioned 25 mole% LiCoO$_2$ cathode of System B. Quite a similar formation of corrosion layers, as seen with the previous cathode, could be seen in this 25 mole% LiCoO$_2$ cathode of System D. However, the notable difference was the presence of slightly higher Ni (about 25%) and Co (about 7%) contents in the iron-rich oxide layer, at the expense of Fe content.
Figure 3.14. SEM micrograph of the cross section of 25 mole% LiCoO$_2$ cathode of System D and AISI 310 current collector, after running about 1200 hours in the lab-cell.

Bergman et al. [91] suggested the possibility of formation a solid solution of LiFeO$_2$ and NiO in the iron-rich oxide layer formed between NiO cathode and AISI 310 current collector. The iron-rich oxide layers reported in this study contain iron oxides with dissolved Ni and small amounts of Co. As shown in the present study (section 3.1.2), up to about 15 mole% of LiCoO$_2$ can easily dissolve and form solid solutions with LiFeO$_2$ and NiO.

Accordingly, it can be suggested the formation of LiFeO$_2$, LiCoO$_2$, and NiO solid solutions in the iron-rich oxide layers seen in the present study. As also shown in the present study (section 3.1.3), the electrical conductivity of the LiFeO$_2$-LiCoO$_2$-NiO ternary oxides increases with the increase of LiCoO$_2$ content up to about 20-25 mole%. Hence, the iron-rich oxide layer (having more Ni and Co contents) formed with 25 mole% LiCoO$_2$ cathode of System D should possess higher electrical conductivity than the iron-rich oxide layer formed with 25 mole% LiCoO$_2$ cathode of System B. This might be a reason for the considerably lower cathodic iR-drop (see Table 3.5) seen with the 25 mole% LiCoO$_2$ cathode of system D, due to possible higher electrical conductivity of its interface layer formed with the current collector, with compared to that of the 25 mole% LiCoO$_2$ cathode of system B.
4. Concluding remarks

In this work, a strategical approach of finding alternative materials in the LiFeO$_2$-LiCoO$_2$-NiO ternary system, to replace the existing cathode of MCFC was undertaken. It has been carried out by investigating the electronic conductivity of the new materials, fabricating porous gas diffusion cathodes out of the preferred materials and evaluating their electrochemical performance, during short-time laboratory-scale cell operation.

The powder synthesis study points out the possibility of preparing powders with appropriate characteristics for MCFC cathode fabrication by the Pechini method. Further, this study indicates the dependence of particle size of LiFeO$_2$-LiCoO$_2$-NiO powders largely on the calcination temperature and the material composition.

The phase analysis performed on the sintered materials indicates the existence of a continues solid solution of the rock-salt structure ($Fm\bar{3}m$) for the LiFeO$_2$-NiO binary system. The existence of LiFeO$_2$-NiO rich solid solutions is found in the LiFeO$_2$-NiO rich ternary materials containing lower LiCoO$_2$ than about 15 - 20 mole%, prepared under systems B (LiFeO$_2$:NiO = 1:1), C (LiFeO$_2$:NiO = 3:1) and D (LiFeO$_2$:NiO = 1:3). The materials with higher LiCoO$_2$ content in these systems show the formation of LiCoO$_2$ rich secondary phase. In LiCoO$_2$ rich materials prepared under the systems E (LiFeO$_2$:NiO = 2:1) and F (LiFeO$_2$:NiO = 1:2), the content of the LiFeO$_2$-NiO rich solid solution phase decreases with increasing LiCoO$_2$ content in the material. Instead, the LiCoO$_2$-rich phase increases at the expense of the LiFeO$_2$-NiO rich solid solution phase.

The electrical conductivity of LiFeO$_2$-NiO binary materials decreases drastically with the increase of LiFeO$_2$ content, indicating the difficulty of using a LiFeO$_2$ rich LiFeO$_2$-NiO binary material for the MCFC cathode. Despite, the electrical conductivity study reveals the ability of preparing materials with adequate electrical conductivity in the LiFeO$_2$-LiCoO$_2$-NiO ternary system. In LiFeO$_2$-NiO rich ternary sub-systems, the electrical conductivity increases to a maximum, followed by a decrease in conductivity with the increase of LiCoO$_2$ content. In general, the materials prepared under System D (LiFeO$_2$:NiO = 1:3) show higher conductivity and also the influence of the LiCoO$_2$ content on conductivity is very significant in this system. The materials prepared under System C (LiFeO$_2$:NiO = 3:1) show relatively low electrical conductivity. The conductivity and also the effect of LiCoO$_2$ content on the conductivity is intermediate in the materials of System B (LiFeO$_2$:NiO = 1:1). In the case of System E (LiFeO$_2$:NiO = 2:1), the conductivity increases to a maximum at around 50 mole% with the decrease of LiCoO$_2$ content, while a continuous increase in conductivity is observed in System F (LiFeO$_2$:NiO = 1:2).

Introduction of poreformers has significantly modified the pore structure of sintered cathodes. A bimodal pore structure, appropriate for the MCFC cathode, could be achieved in sintered cathodes prepared using sub-micron size powders and poreformers. The amount of poreformers significantly affects the electrical conductivity, pore structure and total porosity of sintered cathodes. Further, the cathode fabrication study indicates the nature of the compromise to be made between electrical conductivity, phase purity, mechanical strength, pore structure and porosity in optimization of cathodes for MCFC application.

The 25 mole% LiCoO$_2$ cathodes of System B (LiFeO$_2$:NiO = 1:1) shows an iR-corrected polarization close to that reported for LiCoO$_2$ cathodes. A performance comparable to that of LiCoO$_2$ cathodes is reported with 25 mole% LiCoO$_2$ cathodes of System D (LiFeO$_2$:NiO =
Further, the performance of the 20 mole% LiCoO$_2$ cathode of System D (LiFeO$_2$:NiO = 1:3), is almost comparable to that projected for the NiO cathode in a commercial fuel cell. These cathodes contain LiFeO$_2$-LiCoO$_2$-NiO ternary materials with considerably low NiO contents. An alternative cathode with less NiO content while increasing the contents of LiCoO$_2$ and LiFeO$_2$, which are less soluble in MCFC environment, is generally interesting.

The post cell study shows the existence of higher contents of Ni and Co in the iron-rich corrosion layer formed between the current collector and cathodes of System D (LiFeO$_2$:NiO = 1:3) over the cathodes of System B (LiFeO$_2$:NiO = 1:1). The possibly formed conductive LiFeO$_2$-LiCoO$_2$-NiO solid solution phase in the corrosion layer may have resulted in the lower cathodic iR-drop in the cell run with cathodes of System D.

Altogether, this study reveals the possibility of preparing LiFeO$_2$-NiO-LiCoO$_2$ cathode materials suitable for MCFC application.

5. Suggestions for future work

The existence of LiCoO$_2$ rich phases, besides the LiFeO$_2$-NiO rich solid solution phases, can be seen in the ternary compositions with higher LiCoO$_2$ content. Further, the materials, which possess the highest electrical conductivity in all these studied ternary sub-systems, are multiphase materials. However, the exact correlation between the electrical conductivity and the phases present in the materials is still unknown and this matter should be addressed in future work.

It is suspected that the poor performance of most of the studied cathodes is mainly due to poor electrical conductivity of the cathodes. All the cathodes prepared in this study showed a much lower electrical conductivity, than expected from the high specific electrical conductivity of the cathode material. On the other hand, in some cases, though the cathode shows sufficient electrical conductivity, the electrochemical performance was low probably due to insufficient total porosity together with lack of macro and micro pores. Both these drawbacks can be related to the unoptimized microstructure of the sintered cathodes and the ways of improving the microstructure of cathodes should be investigated.

The more comprehensive electrochemical performance studies together with thorough post-cell studies of tested cathodes, should be performed on the cathodes, which show promising characteristics at the preliminary investigations performed under the present study.

Further, a comprehensive study of solubility of these materials in the electrolyte melt should be performed before making any final assessment on these ternary materials.
6. References