Sol-gel and solid-state fluorination of lithium cobalt oxide for Li-ion secondary batteries

by

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A dissertation submitted in partial fulfillment of the requirements for the degree MSc (Applied Science) in the Faculty of Engineering, Built, Environment and information Technology, University of Pretoria.

Supervisor: Prof PL Crouse

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Declaration

I declare that the thesis which I hereby submit for an MSc (Applied Science) degree at the University of Pretoria is my own work and has not been previously submitted by me for any other degree at this or other institutions.

___________________  ____________________
Ogbeifun Osemeikhian  Date
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Abstract

A series of fluorinated LiCoO$_2$ compounds, LiCoO$_{2-x}$F$_x$ with $x = 0.05 - 0.65$, were synthesised by both a sol-gel and a solid-state method. The sol-gel method utilises LiNO$_3$ and Co(NO$_3$)$_2$.6H$_2$O as Li and Co sources respectively, water and 1-butanol as solvent for the fluoride precursor LiF, and citric acid as the chelating agent. The prepared materials were compared using pXRD, SEM, Raman, TG and DTA analyses. pXRD revealed a secondary phase appearing at $x= 0.25$ in materials prepared by the sol-gel method and as early as $x= 0.08$ in materials prepared by the thermal solid-state method. Materials prepared by the thermal solid-state method required higher temperatures and longer times than materials prepared by the sol-gel method. The results showed that more fluorine can be incorporated in the LiCoO$_2$ structure by the sol-gel than the solid-state method. The secondary phase was identified as lithium oxydifluoride, LiCoOF$_2$. Relatively pure material with stoichiometry could be prepared by both methods. The space was determined as either $C2$ or $P\overline{1}$ and the unit cell dimensions for the two alternatives are reported. This secondary phase has been reported in the literature, but had not been positively identified at the time of submission of this dissertation.

Keywords: fluorinated LiCoO$_2$; LiCoO$_{2-x}$F$_x$; sol-gel fluorination; solid-state fluorination; lithium oxydifluoride.
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List of abbreviations and acronyms

$\mu_{Li}^{int}$ Chemical potential of lithium in positive intercalation electrode

$\mu_{Li}^{graph}$ Chemical potential of lithium in graphite electrode

$a$ Lithium activity

DSC Differential scanning calorimetry

E Volumetric/Gravimetric energy density

EDTA Ethylenediaminetetraacetic acid

DEC Diethyl carbonate

DMC Dimethyl carbonate

EV Electric vehicle

$E_F$ Fermi level

$E_g$ Electrolyte window

EIS Electrochemical impedance spectroscopy

EMC Ethyl methyl carbonate

$F$ Faraday’s constant

FTIR Fourier transform infrared spectroscopy
GIC  Graphite intercalation compound

GITP  Galvanostatic intermittent titration technique

HOMO  Highest occupied molecular orbit

LiMO_2  Layered metal oxide

LTO  Lithium titanate

LUMO  Lowest unoccupied molecular orbital

n  Number of electrons transfer

PC  Propylene carbonate

PITT  Potentiostatic intermittent titration technique

PTC  Positive temperature coefficient

pXRD  Powder X–ray diffraction

Q  Battery capacity

R  Molar gas constant

T  Temperature

TGA  Thermogravimetric analysis

V_e  Electrode potential
1 Introduction

Studies on fluorinated layered transition metal oxide, LiMO₂, for lithium-ion batteries were first undertaken by Kubo and co-workers (Kubo et al., 1997; Amatucci & Pereira, 2007). The studies were on a series of Liₓ₊₁Ni₁₋ₓO₂₋ₓFₓ compounds based on LiNiO₂. Fluorinated LiCoO₂ was also studied (Yonezawa et al., 1998). Furthermore, compounds of the formula Liₓ₊₁Ni₁₋ₓCoₓO₂₋ₓFₓ, where cobalt and fluorine were substituted for nickel and oxygen respectively were investigated (Kubo et al., 1999). It is also possible for more than one transition metal to be partly substituted into a compound: Li[Li₀.2Ni₀.15Co₀.10Mn₀.55]O₂₋ₓFₓ (Amine, Chen & Kang, 2007), LiNi₁/₃Co₁/₃Mn₁/₃O₂₋ₓFₓ (He et al., 2007), Li[Li₀.₂Ni₀.₁₅₋₀.₅ₓCo₀.₁₀Mn₀.₁₅₋₀.₅ₓ]O₂₋ₓFₓ (0 ≤ z ≤ 0.1) (Kang & Amine, 2005).

The layered transition metal oxides, LMO₂ are widely used as cathode materials. Controlled doping of cathode materials with fluorine confers desirable electrochemical and physicochemical properties on the material (Choi et al., 1998). Such properties include good reversibility and capacity retention, stable cycling performance, high tap density (which translates to high volumetric capacity), and thermal stability (Kubo et al., 1997; Kim et al., 2005a; Amine, Chen & Kang, 2007).

The common methods for bulk fluorination – incorporation of fluorine into the crystal structure of materials – are the solid-state and co-precipitation methods. The solid-state method involves firing the required amount of the desired metal and fluorine precursors at high temperatures (>850 °C). Repeated milling, pelleting, and firing of precursors, form the basis of this method (Croguennec et al., 2009). In the co-precipitation method, the precipitate of mixed metal hydroxides or carbonates of Co, Ni, Mn, etc, obtained from the starting materials,
are dehydrated, dried and heated with fluorine precursors (Woo et al., 2007; Min et al., 2013; Yue et al., 2013b; Zhang & Song, 2013).

Surface fluorination of LiCoO₂, LiNiO₂, LiNiₓCo₁₋ₓO₂ materials with gaseous fluorinating agents such as F₂, ClF₂ and NF₃, were investigated by Takashima and co-workers (as reported by Amatucci & Pereira, 2007). As with the bulk fluorination, controlled surface fluorination is reported to result in improved electrochemical performance characteristics such as average discharge capacity, cycling efficiency, and stability.

Sol-gel methods have been applied to synthesis materials with superior electrochemical and physicochemical properties (Oh, Hong & Sun, 1997; Choi et al., 1998; Peng, Wan & Jiang, 1998; Song & Lee, 2002; Zhu et al., 2010). The sol-gel method is however, less frequently applied to fluorinate materials probably due to the low solubility (0.001 – 2.56 g per 100 g of water) of most fluorine precursors, (LiF, NiF₂, MnF₂, MgF₂ and CoF₂) except for the highly soluble ammonium fluoride NH₄F (~100 g per 100 g of water). NH₄F has been used to prepare Li[Li₀.₂Mn₀.₁₅Ni₀.₁₃Co₀.₁₃]O₂₋ₓFₓ, by the sol-gel method (Zheng, Wu & Yang, 2013).

In this study sol-gel and solid-state methods to fluorinate LiCoO₂ layered cathode materials are investigated. The aim of the study is to directly compare the sol-gel and solid state preparation methods and material characteristics obtained with them. The extent to which materials can be fluorinated successfully was also investigated. The sol-gel has the advantages of good stoichiometric control, production of submicron-sized particles, relative short processing time and at lower temperature (Choi et al., 1998; Predoană et al., 2007).
The sol-gel method is solution-based. The technique utilises soluble metal sources, chelating agents, and solvents (1-butanol and water) to dissolve the fluorine precursor. The resulting gel, containing all the required ions, is thermally decomposed. The solid state thermal method on the other hand was prepared by blending the solid, dry starting materials, and heating the mixture to high temperatures.

The materials synthesised were analysed and tested with: pXRD for phase purity and crystal structure; ICP for elemental analyses; vibrational spectroscopy (Raman and FTIR) to study local structure of materials; DTA/TGA to study thermal behaviour of gel and precursor mix from the thermal solid-state; and SEM to study particle size and the morphology of the products.
2 Literature

2.1 Overview of lithium-ion battery technology

Lithium-ion batteries were commercialized in the 1990s (Cook et al., 2013). The term *Lithium-ion*, was coined by Sony Co Ltd, to describe the state of lithium at the anode. This term differentiates such batteries from lithium secondary batteries which have Li metal as their anode (Osaka & Datta, 2000). Intercalation is the principle upon which lithium-ion batteries operate. In this regard, intercalation is the insertion of Li\(^+\) ions into a host structure. The host structure is either the positive cathode or the negative anode. A general description of the lithium-ion battery consists of two electrodes: the anode and cathode; and the lithium-ion-conducting electrolyte. During the charge and discharge processes of the batteries, Li\(^+\) ions *shuttle* between the positive and negative electrodes. The negative electrode acts as a *sink* and the positive electrode as *lithium source*. This process has earned the batteries names such as *shuttle cock*, *rocking chair* or *swing* batteries since lithium ions move back and forth between the cathode and anode (Gummow, Liles & Thackeray, 1993; Lipkowski & Ross, 1994; Liang, Bao & Li, 2006; Ohzuku & Brodd, 2007; Takada, 2013).

The first lithium-ion cell by Sony had LiCoO\(_2\) as the positive electrode and non-graphitic carbon as the negative electrode (Julien, 2000b; Cook et al., 2013). Since the introduction of this battery system, the performance has improved as a result of advances in design and engineering. More improvements are on-going to meet specific market needs (Bruce, 2005). When a lithium-ion battery is first charged in its new state, lithium ions are transferred from the lithium-rich cathode
to the carbon anode; the reverse takes place during discharge (Gummow, Liles & Thackeray, 1993).

Table 2.1 presents some of the criteria for selecting intercalation compounds as positive electrodes and the corresponding advantages.

<table>
<thead>
<tr>
<th>Properties that influence cathode selection, adapted from (Bruce, 1997)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. Ability to intercalate lithium ion</td>
</tr>
<tr>
<td>b. Low Fermi level and Li⁺ site energy → high open-circuit voltage</td>
</tr>
<tr>
<td>c. Capable of accommodating large quantities of lithium per unit formula → High capacity.</td>
</tr>
<tr>
<td>d. Low formula mass → high gravimetric energy density.</td>
</tr>
<tr>
<td>e. Low molar volume → high volumetric energy density.</td>
</tr>
<tr>
<td>f. Sustain high rates of lithium Li⁺ intercalation and de-intercalation → high cell discharge/charge rates.</td>
</tr>
<tr>
<td>g. High reversible lithium Li⁺ intercalation → many charge-discharge cycles</td>
</tr>
<tr>
<td>h. Avoid co-intercalation of solvent-electrolyte.</td>
</tr>
<tr>
<td>i. Easily fabricated into electrode.</td>
</tr>
<tr>
<td>j. Electrode potential varies little with lithium content → cell voltage varies.</td>
</tr>
</tbody>
</table>

### 2.2 Intercalation process

Taking the Sony cell for illustration purposes, the cell is constructed in discharged state and consists of a positive electrode composed of a thin layer of powdered LiCoO₂ mounted on an aluminium foil. The negative electrode is formed from a thin layer of powdered graphite or other carbon material. Upon charging, Li⁺ is de-intercalated from the positive electrode, LiCoO₂, and inserted between the graphene sheets of the graphite, the negative electrode. The reverse process takes place during discharge when load is applied to the battery (Wakihara, 2001; Bruce, 2008). During discharge, when a Li⁺ is inserted back to the cathode from the
anode, compensation electrons are generated which powers the load. This is illustrated in Figure 2.1.

![Figure 2.1](image_url) Representation of Li-ion battery with graphite as anode, LiCoO$_2$ as cathode, separated by a non-aqueous liquid electrolyte LiPF$_6$ ethyl carbonate/dimethyl carbonate (Bruce, 2008).

Oxidation and reduction take place at the cathode and anode respectively driving the charge cycle, as Li$^+$ is extracted from the cathode and intercalated into the negative anode (Thackeray, 1997). The reverse reactions takes place when Li$^+$ move back to the cathode from the anode as shown in the following half-cell reactions:

\[
6C + x\text{Li}^+ + xe^- \rightleftharpoons C_6\text{Li}_x \quad \text{(anode)}
\]  

(2.1)
\[
\text{LiCoO}_2 \Leftrightarrow \text{Li}_{(1-x)}\text{CoO}_2 + x\text{Li}^+ + xe^- \quad \text{(cathode)}
\]  

(2.2)

giving an overall reaction of:

\[
6\text{C} + \text{LiCoO}_2^- \Leftrightarrow C_6\text{Li}_x + \text{Li}_{(1-x)}\text{CoO}_2
\]  

(2.3)

(Fu et al, 2006; Xu et al, 2008).

The amount of Li\(^+\) that moves into and out of the host electrodes and their compensating electrons must be the same to fulfil electro-neutrality. The transition metal oxides in particular are good hosts for intercalation reactions because they possess various oxidation states (Pralong, 2009).

Intercalation reactions also take place in the following transition metal compounds: spinel LiM\(_2\)O\(_4\); olivine LiMPO\(_4\); silicate Li\(_2\)MSiO\(_4\); tavorite LiMPO\(_4\)F and borate LiMBO\(_3\) compounds (M = transition metal) (Xu et al, 2012).

The capacity delivered from an electrode material depends on its molecular weight and on the number of lithium ions reversibly inserted into the structure. The performance of a battery (electrode) is often expressed in terms of the amount of energy it can store per unit mass (gravimetric energy density) and per unit volume (volumetric energy) expressed as:

\[
E = V_e Q
\]  

(2.4)

where \(E\) is the volumetric or gravimetric energy density, \(V_e\) is the electrode potential and \(Q\) is electrical energy stored per unit mass or volume of the
intercalation compound. The units of energy densities are Wh kg\(^{-1}\) or Wh l\(^{-1}\) and \(Q\) is expressed as mAh g\(^{-1}\) or Ah l\(^{-1}\) (Bruce, 1997).

The voltage between the two electrodes is related to the work the cell can deliver on transferring electrons around an external circuit. The cell voltage is also related to the free energy change on transferring Li\(^+\) from one intercalation electrode to the other. Ultimately, the open circuit voltage is related to the difference in the chemical potential of lithium of the two electrodes (Goodenough & Park, 2013), according to the following equation:

\[
V = -\frac{\mu_{Li}^{int} - \mu_{Li}^{graph}}{nF} \tag{2.5}
\]

where \(V\) is the open circuit voltage of the cell, \(\mu_{Li}^{int}\) and \(\mu_{Li}^{graph}\) are the chemical potentials of lithium in the positive intercalation and graphite electrode respectively, \(n\) the number of electrons =1 (since one electron is transferred for each Li\(^+\) ), and \(F\) is the Faraday constant.

Work is done by the cell during discharge when lithium ions are transferred from the anode, where they reside at high potential (high \(\mu_{Li}^{graph}\)) to the cathode, where they have a low chemical potential (low \(\mu_{Li}^{int}\)) (Aydinol & Ceder, 1997; Ceder, Aydinol & Kohan, 1997; Ceder & Aydinol, 1998). During discharge the lithium content changes with accompanying changes in the chemical potential and voltage in each electrode, as \(\mu_{Li} = \mu_{Li}^{0} + RTIna\) , where \(a\) is the activity of lithium (Bruce, 1997). In practice, the potential of the positive electrode is measured against lithium metal, which has an invariant \(\mu_{Li}\) (Aydinol & Ceder, 1997). The chemical
potential of lithium is therefore used as the standard state for lithium in the positive electrode.

Lithium exist as Li\(^+\) ions in intercalation compounds along with their charge-compensating electrons located in the \(d\) levels of the transition-metal ion. Hence the \(\mu_{Li}^{int}\) has two components, the ion and electron contribution according to the equation:

\[
\mu_{Li}^{int} = \mu_{Li}^{int} + \mu_{e^-}^{int}
\] (2.6)

where \(\mu_{Li}^{int}\) and \(\mu_{e^-}^{int}\) represent respectively the chemical potential of lithium ions and electrons. The ion and electron chemical potential include both energy and entropy terms. The compound’s entropy term may be neglected since over most of the composition range entropy changes are small, making a similar contribution to each intercalation compound (Bruce, 1997). The potential of a positive electrode (which translates to cell voltage) depends on the energy of the electrons and the lithium ion in the host compound. The more stable the lithium and/or electron within the structure, the lower the Li\(^+\) site energy and/or Fermi energy, and the larger the thermodynamic potential of the material (Osaka & Datta, 2000). This is important for designing a cathode material.

Inserted electrons in the intercalation host enter at the Fermi level, \(E_F\). This is the electron energy of importance (Bruce, 1997)

\[
E_F = \mu_e
\] (2.7)
The ion contribution to the overall energy is determined predominantly by the site energy of the lithium ion. To maximize electrode potential, choice of compounds with low $E_F$ and high stability (low energy) for Li$^+$ in their sites are preferred. This accounts for the reason why oxides rather than sulphides are favoured as cathode materials of choice (Goodenough & Park, 2013). The lowest $E_F$ which can be achieved for an intercalation compound is determined by the energy corresponding to the top of the valence band of the anion in the compounds. In oxides, the valence band is largely of oxygen 2p character and lies below the corresponding 3p sulphur levels in sulphides. The difference (of more than 2 eV) in $E_F$, allows for potential between 4 V and 5 V vs the Li$^+$/Li couple for transition metal oxide — about 2 V lower in transition metal sulphide (Bruce, 1997; Osaka & Datta, 2000).

In transition metal oxides, the $E_F$ is set by the position of the cation (transition metal) d-orbitals. The operating voltage is expected to increase when moving from 5d to 4d to 3d transition metals and also when moving from $d^n$ to $d^{n+1}$ ($n = 0$ to 6) within the same row of the periodic table (Ueda & Ohzuku, 1994; Julien, 2003b). The lowest d levels are associated with ions from the centre or right of the first transition series (Cr, Fe, Mn, Co, Ni), which exhibit oxidation number of +4 corresponding to the d levels which lie close or just above the top of the oxygen valence band.

Furthermore, the difference in potential between the electrodes is important for this system. The voltage of a cell is equal to the difference in the $E_F$ between electrodes when they are in mutual contact with an electrolyte (Bruce, 1997; Yokokawa et al, 1998).

2.3 Components of lithium-ion battery
Li-ion battery components most commonly encountered in commercial cell are listed in Table 2.2. Figure 2.1 depict these parts for a spirally-wound cylindrical lithium-ion battery. Other battery configurations such as prismatic and coin are also possible. The main components of the lithium-ion battery are the cathode, anode, electrolyte, and separator. The materials that make up these components are briefly described.

![Cross section of lithium-ion battery battery](Osaka & Datta, 2000)

**2.3.1 Cathodes**

Cathode materials that have been widely studied for the lithium-ion battery system are those of layered transition metal oxide (LiMO$_2$) and spinel (LiM$_2$O$_4$) (M = Co, Ni, Mn) (Guo et al, 2002; Santiago et al, 2003). Polyanion compounds such as
phosphates (LiMPO₄); silicates (Li₂SiO₄), fluorophosphates (LiMPO₄F), fluorosulphate (LiMSO₄F), and borates (LiMBO₃) (M = Fe, Mn, Co or Ni), have also been investigated with diverse potentials in these compounds (Gong & Yang, 2011; Xu et al, 2012; Hu, Pang & Zhou, 2013). This classification is brought about by difference in structure, substitution and incorporation of elements into the compounds. Many of such compounds have been synthesised and characterised and more additions are being made as research intensifies to meet cost and diverse applications. Brief descriptions of the crystal structures, properties and examples in each of family of compound are presented.
Table 2.2 Lithium-ion battery components (Osaka & Datta, 2000)

<table>
<thead>
<tr>
<th>S/N</th>
<th>Part</th>
<th>Constituent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cathode</td>
<td>Active material (LiCoO$_2$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Li$_2$CO$_3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Graphite (electro conductive)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PVDF (binder)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al foil (current collector)</td>
</tr>
<tr>
<td>2</td>
<td>Anode</td>
<td>Anode active layer: Hard carbon</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PVDF</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu foil (current collector)</td>
</tr>
<tr>
<td>3</td>
<td>Electrolyte</td>
<td>Solvent: PC, DMC</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Salt: LiPF$_6$</td>
</tr>
<tr>
<td>4</td>
<td>Separator</td>
<td>Polyethylene film</td>
</tr>
<tr>
<td>5</td>
<td>Can (negative electrode)</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Miscellaneous parts:</td>
<td>Gasket, PTC element, safety vent, cap (positive-electrode), positive electrode lead, negative, electrode lead, insulator, mandrel.</td>
</tr>
</tbody>
</table>

LiCoO$_2$, LiNiO$_2$ and LiMnO$_2$ are the most common members of the layered transition metal oxides, LiMO$_2$. They show high specific energy and voltage output. LiCoO$_2$ was the cathode material of choice when Sony commercialized the lithium-ion in the 1990s. It specific capacity is in the range between 130 and 150 mAh g$^{-1}$ (Koksbang et al, 1996; Kızıldaş-Yavuz et al, 2013). This value is just about 50 % of the theoretical value of 280 mAh g$^{-1}$ (Manthiram, Choi & Choi,
Despite the high cost and associated toxicity of cobalt, LiCoO$_2$ still remains attractive to battery makers (Huang et al, 1998).

Though LiNiO$_2$ has drawn attention in addressing of some of the drawbacks of LiCoO$_2$, it suffers from Jahn-Teller distortion and relative difficulty in synthesizing its stoichiometric form, LiNiO$_2$. To surmount this problem, nickel was substituted for a small amount of cobalt to give solid solutions of LiNi$_{1-x}$Co$_x$O$_2$ which combined both properties from LiCoO$_2$ and LiNiO$_2$. Such composition as LiNi$_{0.85}$Co$_{0.15}$O$_2$ was shown to exhibit much higher reversible capacity of 180 mAh g$^{-1}$ with good cyclability than the analogous LiCoO$_2$ system (Kannan & Manthiram, 2003). LiCoO$_2$ and LiNiO$_2$ are isostructural with the layered $\alpha$-NaFeO$_2$ (ordered rock salt structure) with space group $R\bar{3}m$. Figure 2.3 shows infinite slabs of edge-sharing MO$_6$ layers with lithium ion in-between. Their crystal structure is examined in section 2.5.

LiMnO$_2$ has been investigated due to its non-toxicity, reduced cost, and ready availability (Croguennec et al, 1995). LiMnO$_2$ exhibits polymorphism. The polymorphs are the orthorhombic, $\sigma$-LiMnO$_2$, with an ordered rock salt structure with space group $Pmnm$, and the monoclinic $m$-LiMnO$_2$ with space group $C2/m$. 
Figure 2.3  Layered structure of LiMO$_2$ showing transition metal (red) and oxygen (green) atoms forming the layer and lithium ion (blue) sandwiched between the layers

The two polymorphs have the cation ordering of the layered structured α-NaFeO$_2$ (Fu et al, 2005). In the orthorhombic phase, the Mn ion form independent sheets of MnO$_6$ octahedra that are arranged in corrugated (zig-zag) layers. The orthorhombic form is thermodynamically more stable than the $m$-LiMnO$_2$. Stability of these polytypes was found to occur upon iso- and alio-valent substitution of Mn$^{3+}$. There are reports of critical concentrations to attain stability which depend on the substituent. For instance, up to 14 % of the Mn could be replaced by Co in $o$-LiMnO$_2$, yet 5 % Al was found to be enough to stabilize $m$-LiMn$_{1-x}$Al$_x$O$_2$ (Cook et al, 2013).

Cathode materials composed of LiMnO$_2$ can deliver specific discharge capacities of 113-272 mAh g$^{-1}$ within the operating voltage range of 2.0 and 4.5 V (Lu & Wang, 2004). The theoretical discharge capacity is 285 mAh g$^{-1}$. Upon
electrochemical cycling, \( \text{o-LiMnO}_2 \) transforms irreversibly to a material with spinel-like ordering (Julien & Mascot, 2003).

Spinel \( \text{LiMn}_2\text{O}_4 \) is also a good candidate as positive electrode material due to its low cost, high environmental acceptability (non-toxicity) and because it is more easily prepared than nickel and cobalt oxides (Ye \textit{et al}, 2004). It crystallizes in the space group \( \text{Fd3m} \) (Thirunakaran \textit{et al}, 2013). It has a three-dimensional framework (Figure 2.4), for \( \text{Li}^+ \) diffusion (He \textit{et al}, 2005; Luo, Muraliganth & Manthiram, 2009). This material suffers from capacity loss as a result of manganese dissolution into the electrolyte at high temperature from the \( \text{Mn}^{3+/4+} \) redox couple, change of cubic into tetragonal symmetry (Jahn-Teller distortion) occurring at high reduction levels, and changes in crystal lattice arrangement with cycling (Liang, Bao & Li, 2006; Oh \textit{et al}, 2006; Luo, Muraliganth & Manthiram, 2009). The spinel property has been improved by partly substituting different ions for Mn. Synthesis methods that combine anions (S, F, B, Br) and cations (Al, Fe, Cr, Ni, Cu etc) substitutions at the oxygen and manganese sites respectively, have been explored to improve electrochemical performance (Ein-Eli \textit{et al}, 2005; Oh \textit{et al}, 2006; Amaral \textit{et al}, 2010). Surface modification by substances like \( \text{Al}_2\text{O}_3 \) and Ag amongst others, have also been employed to improve electrochemical properties of \( \text{LiMn}_2\text{O}_4 \) (Son, Kim & Park, 2004; Liang, Bao & Li, 2006; Tu \textit{et al}, 2006).
Figure 2.4  Crystal structure of spinel LiM₂O₄ (red: transition metal ion; blue: Li ions) (Xu et al, 2012)

The polyanions is another class of cathode material. Polyanion compounds have tetrahedral structure \((\text{XO}_4)^{n-}\) and their derivatives \((\text{X}_m\text{O}_{3m+1})^{n-}\) (\(\text{X}=\text{P}, \text{S}, \text{As}, \text{or W}\)) with strong covalent bonding, combined with \(\text{MO}_x\) octahedra (\(\text{M}=\)transition metal). Looking at the transition metal oxide structure it is as though the \(\text{O}^-\) anions are replaced by larger size polyanions \((\text{XO})^{n-}\) (Osaka & Datta, 2000; Goodenough, 2013). Olivine phosphates LiMPO₄ are the most widely studied polyanion. Among the olivine phosphates, LiFePO₄ attracts most interests due to its excellent electrochemical properties, low cost, non-toxicity, excellent thermal stability and environmental friendliness (Xu et al, 2012). It is considered one of the most promising cathode materials for use in a plug-in Hybrid Electric Vehicle/Electric Vehicle (PHEV/EV) (Gong & Yang, 2011).
The structure of olivine LiFePO$_4$ is shown in Figure 2.5. It is described as a slightly distorted hexagonal close-packed (hcp) oxygen array resulting in an orthorhombic structure ($D_{2h}^{16}$-space group $Pnmb$). Within the hcp oxygen framework, Li and Fe metal atoms are located in half of the octahedral sites and P atoms are located in 1/8 of the tetrahedral sites. The FeO$_6$ octahedra share corners forming zigzag chains running parallel to the $c$-axis in the alternate $a-c$ planes. These chains are bridged by corner and edge-sharing PO$_4$ tetrahedra to form a host structure with strong three dimensional bonding. The LiO$_6$ octahedra share edges forming linear chains running parallel to the $c$-axis in the other $a-c$ planes. Li$^+$ ions form one dimensional tunnels in the host structure along the [010] direction that run parallel to the planes of corner-sharing FeO$_6$ octahedra (Gong & Yang, 2011; Xu et al, 2012).

There are drawbacks associated with LiFePO$_4$, eg, low electronic conductivity and sluggish Li$^+$ diffusivity, which have been improved upon by reduction in particle size, coating with conducting layers, and doping with cations and anions (Goodenough & Park, 2013; Hong et al, 2013).
Figure 2.5 Polyhedral representation of the crystal structure of olivine LiFePO$_4$, (a) and (b) as viewed along the $b$- and $c$-axis respectively (Gong & Yang, 2011)
2.3.2 Anode

The common anode materials used in lithium batteries are carbonaceous in nature. They are classified as graphite, soft carbon and hard carbon (Figure 2.6) (Wakihara, 2001). Each is capable of intercalating lithium ion in their structure. Graphite, the most popular, is made of sp$^2$ carbon layer sheets (graphene) whose atoms are connected with covalent bonds. The layers are bound together by weak Van der Waals forces; atoms, ion and small groups can enter into the loose connected layers. During charging lithium ions are inserted into the layers to form a graphite intercalation compound (GIC). The theoretical capacity is estimated to be 372 mAh g$^{-1}$.

The soft carbons do not have a well developed layer structure like graphite. There is absence of a perfect crystallinity. Solvents used influence the selection of the carbon electrode to be used. While organic solvents such as propylene carbonate (PC) cannot be used with graphite, as it decomposes, soft carbon can accept the solvent without decomposing. The discharge capacity is limited to the stoichiometry of LiC$_6$ which translates to 372 mAh g$^{-1}$.

The hard carbons are different from both the soft carbon and graphite. It is an aggregate of small crystallites randomly oriented and amorphous, in which there are small irregular spaces (micropores) (Osaka & Datta, 2000). The high discharge capacity of hard carbon is due the crystallites and micropores. The degree of expansion of hard carbon when it absorbs Li$^+$ is relatively small since the distance between layers is already large. The discharge capacity of hard carbon can reach 420 mAh g$^{-1}$ and it is possible to achieve a discharge capacity as high as 600 mAh g$^{-1}$. 
Other attractive anode materials that could replace carbonaceous material is spinel lithium titanate (LTO) \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) (Liu et al., 2013; Mahmoud, Amarilla & Saadoune, 2015). Nanostructured LTO and alloys (nanostructured Sn-Co-C) have been fabricated to obtain materials that intercalate more \( \text{Li}^+ \) and maintain cycling integrity (Bruce, 2008; Etacheri et al., 2011; Fang et al., 2013).

![Image of different types of carbon](image)

Figure 2.6 Types of carbon: (a) soft carbon; (b) hard carbon; (c) graphite

### 2.3.3 Electrolyte

The electrolyte in lithium-ion batteries is the medium through which \( \text{Li}^+ \) is transported between the cathode and anode. They are composed of organic solvent and Li salts. Solvents are chosen that are stable up to the 4.2 V working voltage of the lithium-ion battery. In choosing an appropriate electrolyte, the *window* is such that it allows for thermodynamic stability at equal to or greater than the open voltage (OV). Electrolyte *window* refers to the energy separation \( E_g \), of the lowest
unoccupied molecular orbit (LUMO) and the highest occupied molecular orbit (HOMO) of the electrolyte. The open voltage of the cell is determined by the difference in electrochemical potentials of the anode $\mu_A$ and cathode $\mu_c$ (their Fermi energies $E_F$). Since the electrodes are electron conductors, an anode with a $\mu_A$ above the LUMO of the electrolyte will oxidize the electrolyte. Reduction of the electrolyte occurs when the cathode $\mu_c$ is less than the HOMO of the electrolyte. Oxidation or reduction of the electrolyte can be avoided when a passivation layer that blocks electron transfer is present. Therefore, an anode with $\mu_A$ that matches the LUMO of the electrolyte as well as a cathode with $\mu_c$ that matches the HOMO of the electrolyte are selected (Goodenough & Kim, 2010). Other criteria in selecting electrolytes are solvating power (high dielectric constant), chemical and thermal stability, low viscosity, low melting point and high boiling point, low vapour pressure, and non-flammability (Xu, 2004).

Organic carbonate such as propylene carbonate (PC), ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC) have fairly large electrolyte windows, $E_g$, and are common in use. Due to the highly viscous nature of some solvents which resist ion transport, low viscosity solvents are added. But low viscous liquid solvents have low ionic dissociation. Therefore, in formulating a high dielectric and low viscosity solvent there should be a good balance between ion transport and dissociation. Examples of low viscous solvents are 1, 2-dimethoxyethane, tetrahydrofurane, dioxisolane, diethylcarbonate, dimethyl carbonate.

Lithium salts such as lithium hexafluorophosphate (LiPF$_6$), lithium hexafluoroarsenate (LiAsF$_6$), lithium tetrafluoroborate (LiBF$_4$), lithium trifluoromethanesulphonate (LiCF$_3$SO$_3$), lithium perchlorate (LiClO$_4$) serve as lithium sources in
electrolyte mix (Xu, 2004). Lithium salts dissolved in an organic carbonate constitute a class of *aqueous* electrolyte. There has been a drive towards all-solid (dry) lithium ion battery, where cation mobility is possible through lithium ion-polymer interaction. Notable example is lithium salts mixed with poly(ethyleneoxide) (Scrosati & Garche, 2010; Scheers *et al.*, 2014). Research in electrolytes is a vast field, taking a good proportion of the overall research in the lithium-ion battery system. Though choices may exist, there is not always the freedom to select any solvent if the aim is to keep the characteristics of the battery high.

2.3.4 Separator

The separator prevents direct contact between the cathode and anode thereby preventing short circuit. It allows the transport of ions through its pores. Polyolefins such as polyethylene and polypropylene with micropores are common separators in aqueous batteries, but polymer electrolytes could function both as electrolyte and separator (Arora & Zhang, 2004). They also have a protective function: shutting-down, by melting, when the battery is charged abnormally towards an overvoltage that generates heat inside the cell. The shut-down temperatures of polyethylene and polypropylene are around 120 °C and 130 °C respectively.

2.3.5 Other components

Other components include the PTC (positive temperature coefficient) element, safety vent, added for battery protection and safety. When the PTC is heated over a certain temperature it develops resistance and stops charging and discharging. The cell revives when the temperature decreases. Generation of CO₂ following the
decomposition of Li₂CO₃ during high voltage, increases the internal pressure of the cell. The increased pressure breaks the safety vent and it bends upward. The charging current is cut off as the cathode lead connecting the vent is destroyed. This mechanism keeps the cell temperature less than 50 °C. The small quantity of Li₂CO₃ added to LiCoO₂ electrode material generates the CO₂ (Osaka & Datta, 2000)

2.4 Development of cathode materials

At present, most of the cathode materials for lithium-ion batteries are derivatives of the parent layered metal oxide (LiMO₂), spinel (LiM₂O₄), or olivine (LiMPO₄) structures. Starting with LiMO₂, LiM₂O₄, or LiMPO₂, more materials have been synthesized by partly substituting M in each of them. These materials are doped with cation or anions to form part of the crystal structure of the original compound. Usually, the reason for such doping or substitution is either to reduce cost or to improve on existing properties of the material. These doped materials are isostructural to the parent compounds. Substitution in the layered oxide LiMO₂ and spinel LiMn₂O₄ structures is discussed in the next two sections.

2.4.1 Doping

The two popular layered oxides LiCoO₂ and LiNiO₂ have drawbacks during charge and discharge. Li₅CoO₂ suffers from structural instability and safety problems when the charge voltage exceeds 4.3 V or when the limit of delithiation at x=0.5 is exceeded; and LiNiO₂ has a tendency for non-stoichiometry (Li₁₋ₓNi₁₊ₓO₂) making it difficult to synthesize with consistent quality (Periasamy et al., 2004). The closest to the stoichiometry LiNiO₂ is Li₀.₉₉₆Ni₁.₀₆O₂ (Gover et al., 1999). Non-stoichiometry is caused by Li deficiency and the presence of Ni²⁺ in the Li layer.
which restricts the motion of Li ions in its site. This leads to degradation in charge/discharge properties and poor cycling stability. To solve these problems, the LiNi$_{1-y}$Co$_y$O$_2$ ($0 \leq y \leq 1$) solid solution was developed (Osaka & Datta, 2000). Other substituted layered metal oxides are LiCo$_y$M$_{1-y}$O$_2$ and LiNi$_y$M$_{1-y}$O$_2$ ($M \neq \text{Co, Ni}$) (Rossen, Jones & Dahn, 1992; Reimers et al, 1993; Jones, Rossen & Dahn, 1994).

Surface modification by coating has also been reported: LiCoO$_2$ coated by Fe$_2$O$_3$ and nano-crystalline MgO (Zhao et al, 2004; Hao et al, 2013). In addition, surface modification of LiNiO$_2$ and LiMn$_2$O$_4$ with Al$_2$O$_3$, LaF$_3$, ZnO, SnO$_2$, ZrO$_2$, Li$_2$O·2B$_2$O$_3$ glass and other electro-active oxides, are well reported (Fu et al, 2006; Yi et al, 2009b; Yi et al, 2009a; Takada, 2013; Zhao et al, 2013).

Compounds with three transition metals are popular. A notable one is LiCo$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$, first reported by Ohzuku and Makimura (He et al, 2007; Kızıltas-Yavuz et al, 2013). Variation in terms of the stoichiometric ratio of Co:Ni:Mn is possible, for instance LiCo$_{2/3}$Ni$_{1/6}$Mn$_{1/6}$O$_2$ (Mahmoud et al, 2011).

2.4.2 Bulk doping with fluorine

Fluorine doped in LiMO$_2$, is mostly reported in the literature as F$^-$ substituting for O$^2-$; however, a few authors report this as surface modification (eg Shi et al, 2013b). Kubo et al (1997), studied a series of Li$_{1+x}$Ni$_{1-x}$O$_2$F$_y$, using a solid-state reaction, heating a mixture of Li(OH)·H$_2$O, Ni(OH)$_2$ and LiF in the molar ratio of $(1+x-y):(1-x):y$. Fluorine substitution into the oxygen site, and lithium ion substitution into the nickel site, keep the average oxidation number of nickel greater than 3. Oxidation number less than 3 causes deterioration during charge and discharge when Ni ions enter the lithium layer. They were able to establish
from the study that, unlike LiNiO$_2$ which shows an abrupt phase change with the c-axis shortening around deep charge, the Li$_{1.1}$Ni$_{0.9}$O$_{1.85}$F$_{0.15}$ showed no such change. Again, the Li$_{1.08}$Ni$_{0.92}$O$_{1.9}$F$_{0.1}$ was shown to have superior electrochemical properties compared to LiNiO$_2$ (Kubo et al, 1997).

Kubo et al, (1999) also synthesized a series of Li$_{1+x}$Ni$_{1-x}$Co$_y$O$_{2-y}$F$_y$ by solid-state reaction. LiOH·H$_2$O, LiF and co-precipitated (Ni, Co)(OH)$_2$ powders with molar ratio of 1+x-2z :z:1-x (z = 2x-0.05) were fired at 650 °C in an oxygen environment.

### 2.4.3 Surface fluorination

Surface fluorination has been carried out on LiCoO$_2$, LiNiO$_2$, LiNi$_x$Co$_{1-x}$O$_2$, LiMn$_2$O$_4$ using gaseous fluorinating agents: F$_2$, ClF$_3$, and NF$_3$. Such fluorination was shown to improve electrochemical performance provided it is controlled. Electrochemical behaviour of materials is dependent on fluorination conditions: temperature, fluorinating agent chemistry, and pressure (Takashima, Yonezawa & Ozawa, 2002; Yonezawa, Yamasaki & Takashima, 2004; Amatucci & Pereira, 2007). Fluorination of LiFePO$_4$ has also been investigated (Ueda et al, 2013).

### 2.5 Characterizations of LiMO$_2$

#### 2.5.1 Crystal structure and properties of LiMO$_2$

Layered lithium metal oxide could be indexed based on a hexagonal structure with space group $R\overline{3}m$, isostructural with the rhombohedral $\alpha$-NaFeO$_2$ layered structure. LiMO$_2$ has lithium ions in the 3b, transition metals (Ni and Co) in the 3a, and oxide ions in the 6c Wyckoff sites, represented as [Li]$_{3b}$[Co,Ni]$_{3a}$[O]$_{6c}$ (Rougier, Nazri & Julien, 1997; Schoonman, Tuller & Kelder, 1999; Shin, Shin & Sun, 2006). The ideal structure of the layered LiMO$_2$ has a closed-packed oxygen array
which is slightly distorted from the ideal cubic close packing (rock salt). The structure has a trigonal ($R\bar{3}m$) symmetry and the unit parameters and are usually defined in terms of the hexagonal symmetry settings: $a_{\text{hex}} = 2.83$ Å and $b_{\text{hex}} = 14.09$ Å (Thackeray, 1995; Julien, 2003b).

The ordered rock salt structure of LiCoO$_2$ has edge sharing CoO$_6$ linked to form the CoO$_2$ sheets. The CoO$_2$ sheets/slabs are separated by sheets of octahedrally coordinated lithium ions (LiO$_6$). The sheets of positively charged lithium ions effectively screen and stabilize opposing negatively charged CoO$_2$ sheets (Amatucci, Tarascon & Klein, 1996; Julien, 2000b; Julien et al, 2011; Min et al, 2013). Oxygen planes in the hexagonal structure are stacked in the ABCABC sequence along the $c$-axis and the Co or Ni and Li ions are ordered in respective (111) planes of octahedral sites, shown in Figure 2.7. The oxygen planes contract towards the Co ions resulting in strongly bonded CoO$_2$ sheets separated by layers of Li ions (Ceder & Van der Ven, 1999; Antolini, 2004; Choi & Manthiram, 2005; Manthiram, Choi & Choi, 2006).
Figure 2.7 The α-NaFeO$_2$ type structure with hexagonally stacked close-packed oxygen layer. The metal cations occupy layers of octahedral interstices (Julien, 2000b)

LiCoO$_2$ crystallizes in two phases depending on the temperature of synthesis: low temperature LT-LiCoO$_2$, and high temperature HT-LiCoO$_2$. The LT-LiCoO$_2$ has a cubic spinel structure (space group $Fd\bar{3}m$, point group $O_h$) at 400 °C and the HT-LiCoO$_2$ hexagonal structure (space group $R\bar{3}m$; point group $D_{3d}^5$) at ≥ 800 °C (Julien, 2000b; Song et al, 2001; Lemos, 2004; Mendoza et al, 2004; Fu et al,
There is disordering in the LT-LiCoO$_2$ ($Fd\bar{3}m$) structure in the Co and Li planes associated with distribution of Co and Li in the octahedral sites (Figure 2.8) (Porthault et al., 2012). The cubic closed pack oxygen network of LT-LiCoO$_2$ has alternating cation layers of 0.75 Co, 0.25 Li and 0.75 Li, 0.25 Co composition, perpendicular to each of the four cubic [111] direction. The cell parameters are: $a = 2.8297(6)$ Å and $c = 13.868(4)$ Å with $a/c$ aspect ratio in the range of 4.900 and 5.914, close to that of the ideal cubic close packing oxygen of $cla = 4.899$. (Antolini, 2004).

![Model of the LiCoO$_2$ structure with space group $R\bar{3}m$ (a) and Fd-3m (b) (Porthault et al., 2012).](image)

The HT-LiCoO$_2$ has the ideal $\alpha$-NaFeO$_2$ layered structure with Co and Li planes alternating in the ABCABC oxygen stacking (Shao-Horn et al., 2003; Choi &
Manthiram, 2005; Gabrisch, Kombolias & Mohanty, 2010; Shinova et al, 2011; Levi & Aurbach, 2014). The cell parameter \(a\) (interlayer metal-metal distance) is between 2.815 and 2.816 Å and \(c\) (inter-slab distance) is between 14.05 and 14.06 Å. The value of \(c/a\) ratio is in the range of 4.98 and 5.00, which is larger than that of the ideal cubic closed pack lattice of 4.899 Å (Antolini, 2004).

The two phases HT-LiCoO\(_2\), and LT-LiCoO\(_2\) have different electrochemical characteristics due to cation mixing in the LT-LiCoO\(_2\) (Rossen, Reimers & Dahn, 1993; Schoonman, Tuller & Kelder, 1999; Fu et al, 2009). The \(Fd\bar{3}m\) LiCoO\(_2\) is characterised by slower \(\text{Li}^+\) transport than the \(R\bar{3}m\) LiCoO\(_2\) and is highly reactive towards electrolyte (Porthault et al, 2012). Most of the capacity of LT-LiCoO\(_2\) is in the range between 3.3 and 3.9 V while the HT-LiCoO\(_2\) has most of its capacity in the region of 3.8 to 4.3V.

Over-delithiation results in phase transition from monoclinic to a hexagonal in the voltage range of 4.15 and 4.2 V. This transition causes an abrupt shrinkage along the \(c\)-axis direction accompanied by about 9 % change in volume. This results in cation disorder, where portion of the Li ions enters the 3b sites of Co instead of their normal 3a sites. When \(\text{Li}_{1-x}\text{CoO}_2\) is delithiated below the reversible amount of lithium \(x= 0.5\), electrochemical performance deteriorates by the dissolution of \(\text{Co}^{4+}\) and the \(\text{LiCoO}_2\) particles disintegrate (Fu et al, 2006).

Stoichiometric \(\text{LiNiO}_2\) is difficult to prepare, with loss of Li from the host structure during high temperature calcination as a result of the high vapour pressure of lithium. \(\text{LiNiO}_2\) easily decomposed into Li-deficient compounds \(\text{Li}_d\text{NiO}_{2-d}\) \((0 < d < 1)\) during high temperatures synthesis (Fu et al, 2006). Non-stoichiometry is caused by lithium deficiency and the presence of \(\text{Ni}^{+}\) in the 3a layer sites: \([\text{Li}_{1-x}\text{Ni}_x]_{3a}[\text{Ni}_{1-x}]_{3b}[\text{O}_2]_{6c}\) (Gover et al, 1999; Kalyani & Kalaiselvi, 2005).
During cycling, the behaviour of LiNiO\(_2\) is such that it transforms from the original hexagonal (H1) to monoclinic phase (M) when \(x > 0.5\) in Li\(_{1-x}\)NiO\(_2\). It transits from M to two hexagonal phases (H2+H3) and finally to a single hexagonal H3 phase. The latter two phase changes cause detrimental effects of micro-cracks in each particle, induced by anisotropic lattice changes along the \(a\)- and \(c\)-axis in the initial hexagonal phase, as the capacity decreases markedly (Li, Reimers & Dahn, 1993; Arai \textit{et al}, 1997; Kalyani & Kalaiselvi, 2005; Fu \textit{et al}, 2006).

Generally, the non-stoichiometry of Li\(_{1-x}\)Ni\(_{x+1}\)O\(_2\) results from the instability of Ni\(^{3+}\). The +3 oxidation state is necessary to maintain an ideal layered structure (Kalyani & Kalaiselvi, 2005). The instability of Ni\(^{3+}\) (\(r = 0.56\) Å) would make the compound contain larger Ni\(^{2+}\) (\(r = 0.69\) Å). The similarity in terms of size between Ni\(^{2+}\) (\(r = 0.69\) Å) and Li\(^+\) (\(r=0.72\) Å) favours a three dimensional rock salt type of structure to be formed over an ordered, and two dimensional structure. To obtain good properties of LiNiO\(_2\), synthesis conditions such as providing for lithium and calcining in an oxygen atmosphere to favour the oxidation of Ni\(^{2+}\) to Ni\(^{3+}\) are employed (Rougier \textit{et al}, 1996; Naghash & Lee, 2001).

2.5.2 pXRD of LiMO\(_2\)

pXRD is a common technique employed to characterise the crystal structures of LiMO\(_2\). From the pXRD patterns the crystal structure and any deviation from the ideal structure could easily be guessed. Structural evolution of cathode materials upon cycling has also been studied with pXRD (Morcrette \textit{et al}, 2002). Properties and performance of electrode material are tied to the material structure. Figure 2.9 shows the pXRD pattern of LiCoO\(_2\) by a sol-gel synthesis method using citric acid as the chelating agent mixed with either the acetates or nitrates of the metals (Julien, 2003a).
The pXRD patterns of layered LiMO₂ and their derivatives (when M is partially substituted by transition or other metals) are always indexed by the layered hexagonal α-NaFO₂ belonging to the space group \( R\bar{3}m \). Between 2\( \theta \) values of 10° and 80° peaks attributed to the planes 003, 101, 006, 102, 104, 105, 107, 018, 110, 113, 201, 116 are observed (Ohzuku et al, 1993; Kim et al, 2005b; Yabuuchi et al, 2005).

High quality LiCoO₂ could be compared to the lattice parameters of the JCPDS values of \( a=2.8166\text{Å} \) and \( c=14.052 \text{Å} \) (Amatucci, Tarascon & Klein, 1996). Starting materials, preparation method and conditions (either in oxygen or air) may cause slight difference in lattice parameters of end product (Ohzuku, Ueda & Nagayama, 1993). Ohzuku et al, reported lattice parameters of LiNi\(_{1/2}\)Co\(_{1/2}\)O\(_2\) as \( a=2.84\text{Å}, \ c=14.09 \text{Å} \); LiNiO\(_2\) as \( a=2.88\text{Å}, \ c=14.19\text{Å} \); and LiCoO\(_2\) as \( a=2.81\text{Å}, \ c=14.04\text{Å} \) (Ohzuku, Ueda & Nagayama, 1993; Ohzuku et al, 1993; Ueda & Ohzuku, 1994).

![Figure 2.9](image)

Figure 2.9 XRD pattern of LiCoO\(_2\) prepared by by the sol-gel method using citric acid as chelating agent. The powder was calcined at 800 °C for 4 hours in air (Julien, 2003a)
Materials exhibiting a classical layered structure, found in most LiMO₂ are dominated by a strong Bragg peak located at \(ca\ 2\theta = 19^0\) and with medium intensity peaks at \(36^0\) and \(46^0\). The peak position could slightly differ from these positions depending on the source of radiation in the pXRD measurements (Ohzuku et al., 1993; Bianchi et al., 2001; Singh et al., 2010). The intensity and position of the Bragg peaks is used to index the patterns of the rhombohedral unit cell (\(R\bar{3}m\) space group) in the hexagonal system (Julien, 2003a). The ratios of \(I_{003}/I_{104}\) and/or \(I_{101}/I_{102}\) intensity lines are indicative of the degree of ordering of lithium and transition metal ions in the structure. The splitting of the (006) and (102) as well as the (108) and (110) doublet diffraction lines also indicate desirable properties of the material (Gendron et al., 2003; Zheng et al., 2013; Liao & Xi, 2014). The intensity ratio of \(I_{003}\) to \(I_{004}\) has a critical value of 1.2. A value below this signifies disorder of the layer occupancy, which prevents movement of Li⁺ during cycling (Liao, Duh & Sheen, 2005; Liu et al., 2007; Xia, Tang & Lu, 2008; Yue et al., 2013a). On the other hand, a value of more than 4.9 indicates stabilization of the two dimensional structure and an ordered distribution of lithium and transition metal ions in the lattice (Julien, 2000b; Julien, 2003a; Kızıldaş-Yavuz et al., 2013).

Furthermore, an R (\(R = I_{102} + I_{006} / I_{101}\)) factor value of between 0.39 to 0.53 is an indication of hexagonal ordering (Nithya et al., 2012).

The intensity ratio of (006), (012) and (101) reflections is very sensitive to the stoichiometry of the LiNiO₂ compound. For stoichiometric LiNiO₂, the R value is given by:

\[
R = [I_{006} + I_{012} / I_{101}] 
\]  
(2.7)

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\[
R = [I_{006} + I_{012} / I_{101}] 
\]  
(2.7)
The analytical approximation of $R$ for Li$_x$N$_{1-x}$O$_2$ is given by:

$$R = \frac{4}{3}\left[\frac{(1.6-x)}{x}\right]^2 = 0.485$$

(2.8)

where $x = 0.998$.

A sample that is close to stoichiometry should have an $R$ value calculated from equation 2.7 (using the pXRD data), close to the $R$ value from the analytical approximation of equation of Equation 2.8 (Wang & Navrotsky, 2004).

2.5.3 pXRD of LiMO$_2$ oxyfluorides

Materials that have been successfully doped with fluorine, should be a single phase, isostructural with the un-substituted material, with similar value of intensity ratio $I_{003}/I_{104}$ (Kubo et al, 1997).

Evidence of fluorine substitution can be implied from pXRD data as: change in lattice parameters ($a$ and $c$); changes in certain peaks intensities; and shifts in peak position. Figure 2.10, Figure 2.11, Figure 2.12, Figure 2.13 show pXRD from some studies on fluorinated compounds. Other evidence of fluorine substitution in materials is reduction of the transition metal(s) ions in the structure not evident from pXRD and spectra of fluorine bonding in the compound from XPS measurements.
Figure 2.10 XRD diffraction pattern of LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$-$z$F$_z$ samples with different fluorine content (He et al, 2007)

Figure 2.11 XRD patterns of Li$_{1.05}$(Ni$_{0.5}$Mn$_{0.5}$)$_{0.95}$O$_{2-x}$F$_x$(0 ≤ x ≤ 0.1) materials (Zhang & Song, 2013)
Fluorine substitution in oxyfluorides of layered Li(Ni, Mn, Co)O$_2$ is associated with change in lattice parameters (Croguennec et al, 2009). It is worthwhile to note that the lattice constant $a$ measures the average M-M distance in the basal plane of
the hexagonal structure (M= Li, Ni, Co Mn); and the c constant indicates the ionic radii of the partially reduced transition metal ions (Kim et al, 2005b). Fluorine substitution in layered oxides brings about changes in lattice parameters a and c. Increasing the fluorine content increases the lattice parameters due to charge compensation to maintain electric neutrality of the compound as O\(^{2-}\) is replaced by F\(^-\). During charge compensation the transition metals ions are reduced for instance from: smaller Mn\(^{4+}\)(r = 0.53 Å) to larger Mn\(^{3+}\)(r = 0.645 Å); smaller Co\(^{3+}\) (r = 0.545 Å) to larger Co\(^{2+}\) (r = 0.65 Å); smaller Ni\(^{3+}\)(r = 0.56 Å) to larger Ni\(^{2+}\)(r = 0.645 Å) (Kim et al, 2005b; Zheng, Wu & Yang, 2013). It would be expected that F\(^-\) (of slightly smaller r = 1.33 Å than O\(^{2-}\) r = 1.40 Å) substitution reduces the lattice parameters; but this is overridden by the increased ionic radii of partially reduced transition metal ions. This happen up to a certain value of the fluorine amount (z > 0.1 for LiNi\(_{0.8}\)Co\(_{0.1}\)Mn\(_{0.1}\)O\(_{2-z}\)F\(_z\) as prepared by Kim et al (2005b)). Fluorine content, z, of more than 0.1 results in a decrease in the c axis as the effect of F\(^-\) (having a smaller radius) becomes dominant over the effect of larger ionic radius of transition metal, in determining the c axis. A similar observation was reported for LiNi\(_{1/3}\)Co\(_{1/3}\)Mn\(_{1/3}\)O\(_{2-z}\)F\(_z\): with a fluorine content of z > 0.08 the lattice parameter c decreases due to the effect of replacing O\(^{2-}\) by smaller F, which exceeds the effect of increasing the radii of the reduced transition metal ions (He et al, 2007). In addition, the stronger bond characters between Li and F could contribute to the repulsive force in the oxide making the lattice expand along both a and c axes (Woo et al, 2007).

Weak and broader intensities of the diffraction peaks for Li\(_{1+x}\)Ni\(_{1-x-y}\)Co\(_y\)O\(_{2-x}\)F\(_x\) compounds were reported with increased fluorine content (Kubo et al, 1999). Slight shifts in peaks to lower 2\(\theta\) degree positions of the (003) and (104) peaks were reported for Li\(_{1.05}\)(Ni\(_{0.5}\)Mn\(_{0.5}\))\(_{0.95}\)O\(_{2-x}\)F\(_x\) (0 ≤ x ≤ 0.1) (Zhang & Song, 2013)
and LiNi_{0.8}Co_{0.1}Mn_{0.1}O_{2-z}F_z materials (0 ≤ x ≤ 0.1) (Yue et al, 2013a; Yue et al, 2013b). Peak shifts were also reported for LiNi_{1/3}Co_{1/3}Mn_{1/3}O_{2-x}F_x (0 ≤ x ≤ 0.1) compounds for the (003) and (110) peaks. The (110) peak continuously shifts to lower 2θ angles as the fluorine content increases while the (003) peak initially shifts to a higher 2θ angle when x < 0.05 and then back to lower angles when x > 0.08. These observations were seen as proof of fluorine substitution for oxygen (Kageyama et al, 2006).

The extent of (006)/(102) and (018)/(110) peaks splits was used by Kim et al to show fluorine substitution. For the compounds of LiNi_{0.8}Co_{0.1}Mn_{0.1}O_{2-z}F_z under investigation, they reported clear splits of the (006)/(102) and (018)/(110) peaks up to z = 0.2, an indication of a well-developed layered structure. At z = 0.5, the peaks merge into one and are very difficult to distinguish.

Absence of diffraction peaks of fluorine sources (fluorinating agents) in the final products signals the introduction of fluorine in the materials (Kubo et al, 1999). New diffraction peaks could appear in fluorinated materials (Kageyama et al, 2006). Kageyama et al observed new peaks (impurities) at 38°, 45° and 66° for LiNi_{1/3}Co_{1/3}Mn_{1/3}O_{2-x}F_x (0 ≤ x ≤ 1) at x = 0.5 and presumed the preparation method and the process of achieving electroneutrality in the compound as the reasons for such peaks. They reported that if the fluorine content is over a specific value, in this instance 0.5, the charge compensation through the decrease of the average valence of the transition metals could not meet the requirement of electrical neutrality and a new phase will be formed.

It has been shown that a pure phase can be achieved, with no alteration to the crystal structure up to certain amount of fluorine for specific materials (Kim et al, 2005b; He et al, 2007; Woo et al, 2007; Zhang & Song, 2013).
2.5.4 SEM of oxyfluorides

Fluorine doping changes the morphology and size of material particles (Kim et al., 2005b). With increasing fluorine content, the size of the primary particles increases and becomes better crystallized (He et al., 2007; Woo et al., 2007; Zheng, Wu & Yang, 2013). Most fluorinated materials have spherical morphology made of agglomerates of primary polygons (Yue et al., 2013b). The growth of primary is favoured by increased fluorine content and their shape changes from round-edged to well developed polygon forms (Kim et al., 2005b). Along with changes in morphology, increased tap-density is also reported which led to the conclusion that fluorine substitution not only affects the bulk structure but also alters the surface growth kinetics of products. This increases the pellets size and electrode density (Kim et al., 2005b; Kageyama et al., 2006; Woo et al., 2007).

2.5.5 Vibrational spectroscopy

Vibrational spectroscopy is a useful technique to investigate the local environment of metal ions and surrounding ligands (Nithya et al., 2012). They complement pXRD in the study of cathode materials (Julien, 2003a). Structural evolution and symmetry of crystal structure are also studied with vibrational spectroscopy (Kim, Lee & Kim, 2010). Vibrational spectroscopy is sensitive to short-range environment of oxygen coordination around the cations in the oxide lattice (Julien, 2000b; Castro-García et al., 2003). By factor group analysis, the total irreducible representation for the vibrational modes of LiMO₂ is \( A_{1g} + 2A_{2u} + E_g + 2E_u \). The ungerade modes \( (2A_{2u} + 2E_u) \) are IR-active while the gerade modes \( (A_{1g} + E_g) \) are Raman-active (Julien, 2000a; Baddour-Hadjjean & Pereira-Ramos, 2010). However, more bands and difference in their positions are observed in Raman and
IR measurements depending on the synthesis conditions (phase difference) eg. HT-LiCoO$_2$ and LT-LiCoO$_2$ (Huang & Frech, 1996).

2.5.5.1 Raman Spectra

The Raman active modes ($A_{1g} + E_g$) involve vibrations from oxygen atoms only (Porthault et al, 2012; Tintignac et al, 2012). In the $A_{1g}$ mode two adjacent oxygen layers move rigidly against each other and parallel to the $c$-axis, whereas the atomic displacements in the $E_g$ mode are perpendicular to the $c$-axis, Figure 2.14 (Baddour-Hadjean & Pereira-Ramos, 2010).

Figure 2.14. Atomic displacement of the Raman active modes of hexagonal $R\bar{3}m$ LiCoO$_2$
Recall that LiCoO$_2$ crystallizes in two phases depending on the temperature of synthesis: the LT-LiCoO$_2$ cubic spinel phase with space group $Fd\bar{3}m$ (point group $O_h$) obtained between 550 and 650 °C and the HT-LiCoO$_2$ hexagonal phase with space group $R\bar{3}m$ (point group $D^{5}_{3d}$) obtained between 700 and 900 °C (Fu et al., 2009). Four Raman active modes are observed for LT-LiCoO$_2$ (space group $Fd\bar{3}m$): $A_{1g}$ + $E_g$ + 2$F_{2g}$ at ca 590, 484, 449, 605 cm$^{-1}$. The HT-LiCoO$_2$ has two Raman active modes of $A_{1g}$ + $E_g$ at ca 597 and 487 cm$^{-1}$ (Huang & Frech, 1996; Kang et al., 1999; Okubo et al., 2008; Burba et al., 2009; Fu et al., 2009; Yang et al., 2010), shown in Figure 2.15. As a general rule in layered rock-salt structure, the high frequency band is assigned to the $A_{1g}$ mode, while the low frequency one is of the $E_g$ species.

![Raman scattering of spectra for spinel (a) $Fd\bar{3}m$; (b) hexagonal $R\bar{3}m$ LiCoO$_2$](Porthault et al., 2012).

Raman scattering efficiency of LiNiO$_2$ is weak compared to LiCoO$_2$. This is due to reduction of the rhombohedral distortion in LiNiO$_2$ and increased electrical
conductivity of LiNiO$_2$ resulting in weak optical skin dept of the incident laser beam as shown in Figure 2.16. The intensity of Raman peaks is very sensitive to the long-range order in the NiO$_2$ slabs. With reduction of the rhombohedral distortion in LiNiO$_2$, the $A_{1g}$ and $E_g$ modes of the $R\overline{3}m$ symmetry are degenerate into an $F_{2g}$ which is an inactive vibrational mode for the $Fm\overline{3}m$ symmetry of the rock-salt structure. Non-stiochiometry in LiNiO$_2$ as a result of small amount of extra Ni in the Li slab is evident in the broadening of the $E_g$ mode (Kalyani & Kalaiselvi, 2005).

![Raman spectra of LiMO$_2$ (M = Al, Cr, Co, Ni) layered compounds](image)

Figure 2.16 Raman spectra of LiMO$_2$ (M = Al, Cr, Co, Ni) layered compounds (Julien & Massot, 2004)

### 2.5.5.2 FTIR spectra

The IR active modes $A_{2u} + E_u$ involve vibrations of Co or Ni, O and Li atoms (Figure 2.17). The spectra of LiMO$_2$ are divided into two parts: the low
wavenumber region which contains a well-resolved band at ca 200–300 cm\(^{-1}\), and the high wavenumber region at ca 400–650 cm\(^{-1}\), which contains several bands. The frequency bands in the higher wavenumber region (400–650 cm\(^{-1}\)) are assigned to the Co-O stretching modes of CoO\(_6\) octahedra and O-Co-O bending motions. The isolated frequency band is related to the LiO\(_6\) vibration (Julien & Massot, 2004).

![Diagram](image.png)

**Figure 2.17** Atomic displacement of the IR modes of hexagonal \(R\bar{3}m\) LiCoO\(_2\) (Porthault et al., 2012)

Burba *et al* reported higher frequency bands (of 586 and 600 cm\(^{-1}\)) assigned to Co-O stretching modes of the octahedra, and the lower frequency bands (of 443 and 472 cm\(^{-1}\)) assigned to primarily O-Co-O bending motions; with 650 cm\(^{-1}\) as
shoulder to the 600 cm$^{-1}$ band for conventionally prepared LT-LiCoO$_2$ (Burba et al, 2009).

Figure 2.18 shows the IR spectra of some layered compounds. According to Julien & Massot, a shoulder exists for LiCoO$_2$ spectra at 665 cm$^{-1}$ to the 596 cm$^{-1}$ attributed to an overtone vibration. The far IR peak between 200 − 300 cm$^{-1}$ is related to an asymmetric stretching vibration of LiO$_6$ which is at 241 cm$^{-1}$ and 265 cm$^{-1}$ for LiNiO$_2$ and LiCoO$_2$ respectively. The broadening of high wavenumber IR bands is related to cation-anion bond lengths and/or polyhedral distortion in a material. Broadening of the IR bands in LiNiO$_2$ is associated with distortion of the NiO$_6$ octahedra due to Jahn-Teller effect. In LiCoO$_2$ the shift of IR active modes towards a higher wavenumber could confirm the contraction of elementary unit cell (Julien & Massot, 2004).

![Figure 2.18](image_url) FTIR absorption of LiMO$_2$ (M =Al, Cr, Co, Ni) layered compounds (Julien & Massot, 2004).
2.5.6 Electrochemical characterisation

Electrochemical characteristics of cathode materials are studied using techniques such as galvanostatic charge-discharge characterisation, cyclic voltammetry, electrochemical impedance spectroscopy (EIS), gavanostatic intermittent titration technique (GITT), and potentiostatic intermittent titration technique (PITT). These electrochemical techniques are useful in understanding diffusion, structural changes, and surface phenomena of cathode materials in intercalation processes. Electrochemical processes of Li insertion cathode involve various kinds of interfacial transfer, ion migration through surface films, solid-state diffusion (Li-ions in the host’s lattice), and in many cases, phase transitions. Thermodynamic and kinetic behaviour of insertion electrodes can be analyzed by these electrochemical methods which are much more sensitive to structural variation than pXRD, microscopy (e.g., TEM and SEM) and vibrational spectroscopy (RAMAN and FTIR) (Aurbach, Levi & Levi, 2008). Three of these techniques, namely galvanostatic charge-discharge characterisation, cyclic voltammetry, and electrochemical impedance spectroscopy (EIS), are briefly discussed below.

2.5.6.1 Galvanostatic charge-discharge characteristics

The charge-discharge test is usually carried out at a constant C-rate (current density) and within a given voltage range (operating voltage) to determine the cell capacity at a given potential range. The charge-discharge profile shows the voltage versus the specific capacity (mAh g⁻¹) during the charge and the discharge cycle. The lower and upper voltage limits upon which such test is done are referred to as the lower and upper cut-off voltages respectively. Starting from the lower cut-off voltage, at constant current charging, the voltage is increased to the upper cut-off voltage and the corresponding specific energies are recorded. A plot of the voltage
and capacity is therefore obtained as the charge-discharge curve. During the charge cycle, lithium ions are de-intercalated from the cathode and as more lithium ions are de-intercalated, the specific energy increases. The number of lithium ions that can be sufficiently removed from the cathode determines the specific energy of the cell.

From the galvanostatic charge profile, as illustrated in Figure 2.19, the columbic efficiency (ratio between charge and discharge capacity) for a specified number of cycle(s) and current density is determined. Points C and D represent the specific energy at the end of charge and discharge respectively, from which the columbic efficiency can be determined. The columbic efficiency given by Equation 2.9 (Goodenough, 2013; Goodenough & Park, 2013), relates the capacity consumed during de-intercalation (charging) D, and the power returned upon intercalation (discharging) C.

\[
\text{Columbic efficiency} = \left( \frac{C}{D} \cdot 100 \right) \%
\]  
\hspace{1cm} (2.9)

The irreversible capacity is given as the difference between C and D.
Cyclic performance can also be obtained from a plot of the specific capacity versus the number of cycles as shown in Figure 2.20. The different curves A, B and C represent different characteristics after several cycles, each exhibiting different capacity retention. For instance curve A shows a better performance, having a higher specific capacity and minimal decrease in specific capacity upon cycling compared to B and C.
Rate capability testing can also be determined on a cathode material which gives the voltage profile at various C-rates in a specified potential range.

In these experiments, parameters such as current density, cut-off voltage, number of cycles (n), and temperature are usually specified.

### 2.5.6.2 Cyclic voltammetry

Study of reversibility of electrode and redox couples is done by cyclic voltammetry. Electrodes are usually scanned for redox couples at a specified scan rate (usually 0.1 mV/s for lithium-ion battery systems) between two sets of voltage ranges (working voltage range), encompassing most of the electrode reactions. For a positive potential scan, the potential is increased to the upper value; for a negative scan, the potential is reduce from the upper towards the lower voltage limit. During the potential scans, the current at the electrode is measured, and a plot of the current versus potential, a voltammogram, is obtained, (Figure 2.21).
During the positive scan when the applied potential becomes increasingly positive, oxidation of electroactive species occurs. This is accompanied by increased anodic current and a peak formed. The current decays after the peak. In the reverse scan, the oxidized species are reduced back to their reduced state, which creates the cathodic current.

From the voltammogram, the nature of the redox peaks (sharp or round), intensity and width, voltage separation $\Delta E$, and symmetry give useful information on the nature of the electrode under investigation. Sharper, higher, and more symmetrical redox peaks, indicate improved electrode response rate and higher electrochemical activities. Also, smaller value of $\Delta E$ indicates a decrease in polarization, desired in electrode materials (Huang et al, 2013; Shi et al, 2013b; Zhao et al, 2013). This technique identifies the reversible couple, measures rate constants, and transfer coefficient of electrode process. A reversible, diffusion-controlled reaction, exhibits an approximately symmetrical pair of current peaks as shown in figure Figure 2.22a. In ideal case, the value of $\Delta E$ is close to zero. Quasi-reversible processes have current peaks that are more separated, and the shape of the peaks are less sharp and more rounded as shown in Figure 2.22b. A completely irreversible electrode process produces a single peak as shown in the Figure 2.22c. More than one oxidation and reduction peaks are possible, in which case there exist more than one electroactive species or different oxidation potential (levels) of the same species (Liang, Bao & Li, 2006).
Figure 2.21 Shape of a typical voltammogram

Figure 2.22 Cyclic voltammograms of a) reversible; b) quasi-reversible, and c) irreversible processes

2.5.6.3 Electrochemical Impedance Spectroscopy (EIS)

EIS is used to study impedance at the electrode-electrolyte interface and resistance of the interface film formed on electrode surfaces. In EIS measurement, a small
AC signal of between 5 mV and 10 mV is imposed on an electrochemical cell at a finite DC bias potential or open current voltage (OCV), and the impedance $Z$ (equivalence of resistance $R$ in DC measurement) is determined over a wide range of frequencies, normally between 0.01 Hz and 1 MHz.

Real ($Z''$) and imaginary ($Z'''$) parts of impedance data are plotted on a complex plane to obtain a semi-circle called a Nyquist plot. Impedance spectra are combination of depressed semicircles: the high-frequency semi-circle (HFS); medium-frequency semi-circle (MFS) and straight lines in the low-frequency semi-circle (LFS) as depicted in Figure 2.23. In the case for a lithium-ion system, the HFS relates to Li$^+$ migration through the surface film ($R_{st}$) covering the active material. The MFS is attributed to charge-transfer of Li$^+$ ($R_{ct}$) across the interface between the surface film and the active material and the LFS is related to the Li$^+$ diffusion process in the active material, whose slope is related to Li$^+$ diffusion (Warburg diffusion) in the bulk electrode (Kim, Park & Sun, 2003; Levi & Aurbach, 2005; Muto et al, 2012; Zheng, Wu & Yang, 2013).
2.5.7 Other methods

In addition to the above techniques, other techniques applied to study cathode material are: differential scanning calorimetry (DSC); thermogravimetric analysis (TGA); differential thermal analysis (DTA); differential calorimetry, scanning electron microscopy (SEM); transmission electron microscopy (TEM); X-ray photoelectron spectroscopy (XPS); ethylenediaminetetraacetic acid (EDTA) titration; inductively coupled plasma spectroscopy (ICP-OES); and ion chromatography. Each of these analytical techniques is either used to study intermediate steps or final product of a synthesis process.

DSC, TGA, DTA are applied to study cathode material thermal behaviour, both in the charged and discharge state. They are also used to study formation of products from starting materials, e.g. decomposition gel in sol-gel method. SEM is useful in studying material surface in surface coating or doping of electrode materials. ICP-
OES, EDTA and ion chromatography are used for elemental analysis in prepared materials.

2.5.8 Synthesis methods for cathode materials

Several methods are available for the synthesis of cathode materials. The common synthesis methods are the solid and wet/soft chemistry (sol-gel and coprecipitation) methods. Among the wet chemistry methods, sol-gel dominates due to the good properties of products. The solid-state method involves heating a mixture of starting materials to promote diffusion in the solid-state. The sol-gel method, on the other hand, uses chelating agents that help to disperse the metal atoms at atomic scale. Therefore, it requires less heating time. The sol-gel and solid-state methods are discussed in the next two sections. Other synthesis methods are: hydrothermal (Burukhin et al, 2002; Wei et al, 2013); supercritical drying (Lee et al, 2010); spray decomposition (Li et al, 2000); melt impregnation (Xia et al, 1995; Tu et al, 2006); chemical lithiation (Jung et al, 2010); freeze drying (Shlyakhtin et al, 2004; Shi et al, 2013a); epitaxial growth (Shiraki et al, 2014); and electrospinning (Fu, Ma & Qin, 2005; Shao et al, 2006; Ding et al, 2009).

2.5.9 Solid-state methods

The solid-state method is widely used to synthesize ceramics. It involves intimate grinding, mixing and sintering of stoichiometric mixtures of starting materials. Generally, the starting materials are thoroughly ground and/or milled, then subjected to heat treatment. The mixture may be reground and/or pelletized, then sintered at higher or the same temperature as the pre-heating treatment. This method is economical, efficient, and easy to scale up. The ills associated with the solid-state method are inhomogeneity, irregular morphology, large particle size
distribution, long heating time followed by several grinding and annealing processes, and poor control of stiochiometry of the final products. As a result, material performance may be poor (Zhang et al, 2003; He et al, 2005).

### 2.5.10 Sol-gel method

In this method, precursors are dissolved in solvents and a sol (or solution) evolved gradually towards the formation of gel-like network containing both a liquid phase and a solid phase during evaporation. The gel is then dried and sintered at higher temperature (Gong & Yang, 2011). The sol-gel method is attractive because it overcomes the shortcomings of the solid-state method of long heating time and high temperature to get uniform and good products (Liu et al, 2004). The basic processing step of the sol-gel method is summarized as follows:

Precursor → hydrolysis → reactive monomer → condensation → sol gelation → gel → further treatment.

This synthesis route allows for variations of precursor, solvent and ligands (Fu et al, 2005).

In order to achieve uniformity and control particle size, organic compounds with hydrophilic functional groups like hydroxides and carboxylates are added as carrier. Small molecules such as ascorbic, malic, succinic, tartaric, citric, poly-acrylic and other organic acids are also used. The metal ion (e.g. Li⁺, Co²⁺, Ni²⁺,) interaction with the polar side groups leads to a homogenous distribution of the metals ions in the obtained gel and enhanced crystallization process during the heat-treatment. The advantages of the sol-gel method are better homogeneity, shorter heating time, regular morphology, less impurities, larger surface area, and
good control of stiochiometry which impacts positively on the electrochemical and physical properties of cathode materials.

2.5.11 Fluorination methods

Fluorination methods are not different from the methods discussed so far. The additional material that is required is the source of fluorine in such synthesis. Common sources of fluorine in bulk fluorination are LiF, NiF₂, NH₄F, NaF and KF (Naghash & Lee, 2001; Croguennec et al, 2009; Shi et al, 2013b; Yue et al, 2013a; Yue et al, 2013c; Zheng, Wu & Yang, 2013). In bulk fluorination using the solid-state method, LiF is usually fired with metal sources such as LiOH.H₂O, Co(OH)₂ and Ni(OH)₂.

In surface fluorination, fluorinating agents such as F₂, ClF₃ and NF₃ are used. The already synthesized material is exposed to these fluorinating agents with varying condition such of temperature and pressure. Takashima and co-workers carried out surface fluorination of LiCoO₂, LiNiO₂, LiNiₓCo₁₋ₓO₂ and LiMn₂O₄ (Yonezawa, Yamasaki & Takashima, 2004; Amatucci & Pereira, 2007).
3 Experimental

3.1 Chemicals and reagents

Citric acid (C₆H₈O₇·6H₂O), cobalt nitrate hexahydrate, lithium nitrate (LiNO₃, 99.99 %) and lithium fluoride (LiF) were purchased from Merck. Ammonia solution (NH₄·H₂O, 25 %), 1-butanol (99.9 %), lithium hydroxide monohydrate (LiOH·H₂O, ≥98.0 %); cobalt (II, III) oxide (Co₃O₄) were purchased from Sigma-Aldrich.

3.2 Sol-gel synthesis

3.3 Preparation of LiCoO₂

The material requirements for the sol-gel synthesis of LiCoO₂ are presented in Table 3.2.1

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Theoretical Amount Required</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNO₃</td>
<td>0.24 g</td>
</tr>
<tr>
<td>Co(NO₃)₂·6H₂O</td>
<td>1 g</td>
</tr>
<tr>
<td>H₂O (Distilled)</td>
<td>50 ml</td>
</tr>
<tr>
<td>C₆H₈O₇·H₂O (Citric Acid Monohydrate)</td>
<td>2.91 g</td>
</tr>
<tr>
<td>Ammonia solution (25 %)</td>
<td>Variable</td>
</tr>
</tbody>
</table>

The LiNO₃ and Co(NO₃)₂·6H₂O were dissolved together in 50 ml of water to obtain a solution with a 1:1 ratio of Li⁺ to Co²⁺. Citric acid was dissolved in 50 ml of water and added to the metal nitrate solution while stirring. The mixture was kept at ~25 °C while stirring for 30 minutes to allow homogenous mixing to occur.
The final solution was evaporated at 80 °C to produce a gel. Ammonia solution was periodically added to maintain pH between 4.5 and 5.5. The gel was heated in a furnace to 400 °C at 2 °C min\(^{-1}\) (3 h 20 min) and held for 5 h to remove the organic materials. The fluffy mass obtained is slightly ground and heated to 750 °C at 2 °C min\(^{-1}\) and held for 10 h to obtain the final product.

3.4 Preparation of LiCoO\(_{2-x}\)F\(_{x}\) (0.05 \(\leq\) x \(\leq\) 0.65)

The series of LiCoO\(_{2-x}\)F\(_{x}\) compounds synthesised is presented in Table 3.2.2.

<table>
<thead>
<tr>
<th>X</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.65</td>
<td>LiCoO(<em>{1.35})F(</em>{0.65})</td>
</tr>
<tr>
<td>0.55</td>
<td>LiCoO(<em>{1.45})F(</em>{0.55})</td>
</tr>
<tr>
<td>0.45</td>
<td>LiCoO(<em>{1.55})F(</em>{0.45})</td>
</tr>
<tr>
<td>0.35</td>
<td>LiCoO(<em>{1.65})F(</em>{0.35})</td>
</tr>
<tr>
<td>0.25</td>
<td>LiCoO(<em>{1.75})F(</em>{0.25})</td>
</tr>
<tr>
<td>0.15</td>
<td>LiCoO(<em>{1.85})F(</em>{0.15})</td>
</tr>
<tr>
<td>0.08</td>
<td>LiCoO(<em>{1.98})F(</em>{0.08})</td>
</tr>
<tr>
<td>0.05</td>
<td>LiCoO(<em>{1.95})F(</em>{0.05})</td>
</tr>
</tbody>
</table>

The molar ratio of (1-x):1: x for LiNO\(_3\), Co(NO\(_3\))\(_2\).6H\(_2\)O and LiF respectively was used all through.

The material requirements for the sol-gel synthesis of LiCoO\(_{1.35}\)F\(_{0.65}\) through to LiCoO\(_{1.95}\)F\(_{0.05}\) are given in Table 3.2.3, Table 3.2.4, Table 3.2.5, Table 3.2.6, Table 3.2.7, Table 3.2.8, Table 3.2.9, Table 3.2.10 below
### Table 3.2.3 Materials for LiCoO$_{1.35}$F$_{0.65}$ synthesis

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Theoretical Amount Required</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNO$_3$</td>
<td>0.083 g</td>
</tr>
<tr>
<td>Co(NO$_3$)$_2$.6$H_2$O</td>
<td>1 g</td>
</tr>
<tr>
<td>LiF</td>
<td>0.058 g</td>
</tr>
<tr>
<td>H$_2$O (Distilled)</td>
<td>70 ml</td>
</tr>
<tr>
<td>1-butanol</td>
<td>40 ml</td>
</tr>
<tr>
<td>C$_6$H$_8$O$_7$.H$_2$O (Citric Acid Monohydrate)</td>
<td>2.89 g</td>
</tr>
<tr>
<td>Ammonia solution (25%)</td>
<td>Variable</td>
</tr>
</tbody>
</table>

### Table 3.2.4 Materials for LiCoO$_{1.45}$F$_{0.55}$ synthesis

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Theoretical Amount Required</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNO$_3$</td>
<td>0.91 g</td>
</tr>
<tr>
<td>Co(NO$_3$)$_2$.6$H_2$O</td>
<td>8.56 g</td>
</tr>
<tr>
<td>LiF</td>
<td>0.049 g</td>
</tr>
<tr>
<td>H$_2$O (Distilled)</td>
<td>70 ml</td>
</tr>
<tr>
<td>1-butanol</td>
<td>40 ml</td>
</tr>
<tr>
<td>C$_6$H$_8$O$_7$.H$_2$O (Citric Acid Monohydrate)</td>
<td>12.35 g</td>
</tr>
<tr>
<td>Ammonia solution (25%)</td>
<td>Variable</td>
</tr>
</tbody>
</table>

### Table 3.2.5 Materials for LiCoO$_{1.55}$F$_{0.45}$ synthesis

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Theoretical Amount Required</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNO$_3$</td>
<td>0.13 g</td>
</tr>
<tr>
<td>Co(NO$_3$)$_2$.6$H_2$O</td>
<td>1 g</td>
</tr>
<tr>
<td>LiF</td>
<td>0.04 g</td>
</tr>
<tr>
<td>H$_2$O (Distilled)</td>
<td>70 ml</td>
</tr>
<tr>
<td>1-butanol</td>
<td>40 ml</td>
</tr>
<tr>
<td>C$_6$H$_8$O$_7$.H$_2$O (Citric Acid Monohydrate)</td>
<td>2.89 g</td>
</tr>
<tr>
<td>Ammonia solution (25%)</td>
<td>Variable</td>
</tr>
</tbody>
</table>
Table 3.2.6 Materials for LiCoO$_{1.65}$F$_{0.35}$ synthesis.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Theoretical Amount Required</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNO$_3$</td>
<td>0.15 g</td>
</tr>
<tr>
<td>Co(NO$_3$)$_2$·6H$_2$O</td>
<td>1 g</td>
</tr>
<tr>
<td>LiF</td>
<td>0.031 g</td>
</tr>
<tr>
<td>H$_2$O (Distilled)</td>
<td>70 ml</td>
</tr>
<tr>
<td>1-butanol</td>
<td>40 ml</td>
</tr>
<tr>
<td>C$_6$H$_8$O$_7$·H$_2$O (Citric Acid Monohydrate)</td>
<td>2.86 g</td>
</tr>
<tr>
<td>Ammonia solution (25%)</td>
<td>Variable</td>
</tr>
</tbody>
</table>

Table 3.2.7 Materials for LiCoO$_{1.75}$F$_{0.25}$ synthesis

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Theoretical Amount Required</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNO$_3$</td>
<td>0.18 g</td>
</tr>
<tr>
<td>Co(NO$_3$)$_2$·6H$_2$O</td>
<td>1 g</td>
</tr>
<tr>
<td>LiF</td>
<td>0.022 g</td>
</tr>
<tr>
<td>H$_2$O (Distilled)</td>
<td>70 ml</td>
</tr>
<tr>
<td>1-butanol</td>
<td>40 ml</td>
</tr>
<tr>
<td>C$_6$H$_8$O$_7$·H$_2$O (Citric Acid Monohydrate)</td>
<td>2.89 g</td>
</tr>
<tr>
<td>Ammonia solution (25%)</td>
<td>Variable</td>
</tr>
</tbody>
</table>

Table 3.2.8 Materials for LiCoO$_{1.85}$F$_{0.15}$ synthesis.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Theoretical Amount Required</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNO$_3$</td>
<td>0.20 g</td>
</tr>
<tr>
<td>Co(NO$_3$)$_2$·6H$_2$O</td>
<td>1 g</td>
</tr>
<tr>
<td>LiF</td>
<td>0.013 g</td>
</tr>
<tr>
<td>H$_2$O (Distilled)</td>
<td>70 ml</td>
</tr>
<tr>
<td>1-butanol</td>
<td>40 ml</td>
</tr>
<tr>
<td>C$_6$H$_8$O$_7$·H$_2$O (Citric Acid Monohydrate)</td>
<td>2.88 g</td>
</tr>
<tr>
<td>Ammonia solution (25%)</td>
<td>Variable</td>
</tr>
</tbody>
</table>
Table 3.2.9 Materials for LiCoO$_{1.92}$F$_{0.08}$ synthesis.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Theoretical Amount Required</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNO$_3$</td>
<td>0.212 g</td>
</tr>
<tr>
<td>Co(NO$_3$)$_2$.6H$_2$O</td>
<td>1 g</td>
</tr>
<tr>
<td>LiF</td>
<td>0.007 g</td>
</tr>
<tr>
<td>H$_2$O (Distilled)</td>
<td>70 ml</td>
</tr>
<tr>
<td>1-butanol</td>
<td>40 ml</td>
</tr>
<tr>
<td>C$_6$H$_8$O$_7$.H$_2$O (Citric Acid Monohydrate)</td>
<td>2.9 g</td>
</tr>
<tr>
<td>Ammonia solution (25%)</td>
<td>Variable</td>
</tr>
</tbody>
</table>

Table 3.2.10 Materials for LiCoO$_{1.95}$F$_{0.05}$ synthesis.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Theoretical Amount Required</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNO$_3$</td>
<td>0.23 g</td>
</tr>
<tr>
<td>Co(NO$_3$)$_2$.6H$_2$O</td>
<td>1 g</td>
</tr>
<tr>
<td>LiF</td>
<td>0.0044 g</td>
</tr>
<tr>
<td>H$_2$O (Distilled)</td>
<td>70 ml</td>
</tr>
<tr>
<td>1-butanol</td>
<td>40 ml</td>
</tr>
<tr>
<td>C$_6$H$_8$O$_7$.H$_2$O (Citric Acid Monohydrate)</td>
<td>2.90 g</td>
</tr>
<tr>
<td>Ammonia solution (25%)</td>
<td>Variable</td>
</tr>
</tbody>
</table>

The LiNO$_3$ and Co(NO$_3$)$_2$.6H$_2$O are dissolved together in 50 ml of water; LiF was dissolved in a mixture of 20 ml of water and 40 ml of 1-butanol and stirred. Citric acid was dissolved in 50 ml of water and added to the solution while stirring. The mixtures are kept at ~25 °C while stirring for 30 min to allow homogenous mixing to occur.

The final solution is evaporated at 80 °C to produce a gel. Ammonia solution is periodically added to maintain pH between 4.5 and 5.5 during evaporation. The gel is heated in a furnace under air atmosphere, to 400 °C at 2 °C min$^{-1}$(3 h 20 min) and held for 5 hrs, to decompose the organic materials. The fluffy mass obtained is
slightly ground and heated to 750 °C at 2 °C min⁻¹ and held for 10 h to obtain the final product.

4 Solid-State synthesis of LiCoO₂

4.1 Preparation of LiCoO₂

To obtain Li and Co mole ratio of 1:1 in the compound, 7.84 g and 15 g of LiOH·H₂O and Co₃O₄ respectively are properly mixed in a planetary ball mill at 400 rpm for 40 min. The mixture is calcined at 800 °C for 40 h. The calcined sample is ground and re-calcined at 800 °C for 12 h.

4.2 Preparation of LiCoO₂₋ₓFx (0.05 ≤ x ≤ 0.65)

The series of LiCoO₂₋ₓFx synthesized is presented in Table 4.1. The same mixing and heating programme described for LiCoO₂ preparation in section 5.1 was used for each member compound.

<table>
<thead>
<tr>
<th>X</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.65</td>
<td>LiCoO₁.3xF₀.65</td>
</tr>
<tr>
<td>0.55</td>
<td>LiCoO₁.4xF₀.55</td>
</tr>
<tr>
<td>0.45</td>
<td>LiCoO₁.5xF₀.45</td>
</tr>
<tr>
<td>0.35</td>
<td>LiCoO₁.6xF₀.35</td>
</tr>
<tr>
<td>0.25</td>
<td>LiCoO₁.7xF₀.25</td>
</tr>
<tr>
<td>0.15</td>
<td>LiCoO₁.8xF₀.15</td>
</tr>
<tr>
<td>0.08</td>
<td>LiCoO₁.9xF₀.08</td>
</tr>
<tr>
<td>0.05</td>
<td>LiCoO₁.9xF₀.05</td>
</tr>
</tbody>
</table>
The molar ratio of (1-x):1:x for LiOH·H₂O, Co₃O₄ and LiF respectively was used all through.

The material requirements for the solid-state synthesis of LiCoO₁.₃₅F₀.₆₅ through to LiCoO₁.₉₅F₀.₀₅ are given in Table 4.2, Table 4.3, Table 4.4, Table 4.5, Table 4.6, Table 4.7, Table 4.8, Table 4.9 below

<table>
<thead>
<tr>
<th>Material</th>
<th>Amount (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiOH·H₂O</td>
<td>0.55</td>
</tr>
<tr>
<td>Co₃O₄</td>
<td>3.00</td>
</tr>
<tr>
<td>LiF</td>
<td>0.63</td>
</tr>
</tbody>
</table>

Table 4.2 Materials for LiCoO₁.₃₅F₀.₆₅ synthesis

<table>
<thead>
<tr>
<th>Material</th>
<th>Amount (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiOH·H₂O</td>
<td>0.71</td>
</tr>
<tr>
<td>Co₃O₄</td>
<td>3.00</td>
</tr>
<tr>
<td>LiF</td>
<td>0.53</td>
</tr>
</tbody>
</table>

Table 4.3 Materials for LiCoO₁.₄₅F₀.₅₅ synthesis

<table>
<thead>
<tr>
<th>Material</th>
<th>Amount (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiOH·H₂O</td>
<td>0.86</td>
</tr>
<tr>
<td>Co₃O₄</td>
<td>3.00</td>
</tr>
<tr>
<td>LiF</td>
<td>0.44</td>
</tr>
</tbody>
</table>

Table 4.4 Materials for LiCoO₁.₅₅F₀.₄₅ synthesis
Table 4.5 Materials for LiCoO$_{1.65}$F$_{0.35}$ synthesis

<table>
<thead>
<tr>
<th>Material</th>
<th>Amount (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiOH·H$_2$O</td>
<td>1.02</td>
</tr>
<tr>
<td>Co$_3$O$_4$</td>
<td>3.00</td>
</tr>
<tr>
<td>LiF</td>
<td>0.34</td>
</tr>
</tbody>
</table>

Table 4.6 Materials for LiCoO$_{1.75}$F$_{0.25}$ synthesis

<table>
<thead>
<tr>
<th>Material</th>
<th>Amount (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiOH·H$_2$O</td>
<td>1.18</td>
</tr>
<tr>
<td>Co$_3$O$_4$</td>
<td>3.00</td>
</tr>
<tr>
<td>LiF</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Table 4.7 Materials for LiCoO$_{1.83}$F$_{0.15}$ synthesis

<table>
<thead>
<tr>
<th>Material</th>
<th>Amount (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiOH·H$_2$O</td>
<td>1.33</td>
</tr>
<tr>
<td>Co$_3$O$_4$</td>
<td>3.00</td>
</tr>
<tr>
<td>LiF</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Table 4.8 Material for LiCoO$_{1.92}$F$_{0.08}$ synthesis

<table>
<thead>
<tr>
<th>Material</th>
<th>Amount (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiOH·H$_2$O</td>
<td>1.44 g</td>
</tr>
<tr>
<td>Co$_3$O$_4$</td>
<td>3.00</td>
</tr>
<tr>
<td>LiF</td>
<td>0.078</td>
</tr>
</tbody>
</table>
Table 4.9 Materials for LiCoO$_{1.95}$F$_{0.05}$ synthesis

<table>
<thead>
<tr>
<th>Material</th>
<th>Amount (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiOH·H$_2$O</td>
<td>1.49</td>
</tr>
<tr>
<td>Co$_3$O$_4$</td>
<td>3.00</td>
</tr>
<tr>
<td>LiF</td>
<td>0.048</td>
</tr>
</tbody>
</table>

Each compound was prepared as described in Section 4.1

4.3 Preparation of LiCoOF$_2$

The materials for the preparation of the oxyfluoride are listed in Table 4.10 and Table 4.11 via the sol-gel and solid state methods respectively.

Table 4.10 Materials for LiCoOF$_2$ synthesis

<table>
<thead>
<tr>
<th>Material</th>
<th>Amount (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNO$_3$</td>
<td>0.50</td>
</tr>
<tr>
<td>CoF$_2$</td>
<td>0.70</td>
</tr>
</tbody>
</table>

Table 4.11 Materials for LiCoOF$_2$ synthesis

<table>
<thead>
<tr>
<th>Material</th>
<th>Amount (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiOH·H$_2$O</td>
<td>1.00</td>
</tr>
<tr>
<td>CoF$_2$</td>
<td>0.62</td>
</tr>
</tbody>
</table>
4.4 Equipment and analytical methods

Samples were analyzed using a PANalytical X’Pert Pro powder diffractometer in θ-θ configuration with an X’Celerator detector and variable divergence and fixed receiving slits with Fe-filtered Co-Kα radiation (λ=1.789Å). Phases were identified using X’PertHighscore plus software.

Micrographs of the samples were taken with Zeiss Utra Plus SEM.

Raman spectra were collected using a Jobin Yvon TX6400 spectrometer.

TGA and DTA data of decomposed gel and the mixtures from the thermal solid method were recorded with a Hitachi STA 7300 TGA-DTA.

A Carbolite muffle furnace with VT 9630 controller was used for the heating.

A Spectro Arcos ICP-OES was used for elemental analyses of Co and Li.

A Mettler Toledo® pH/ion meter S220 (fluoride ion selective electrode) was used to determine the fluoride amount in the samples. In the analyses, 100 ppm of solution from the samples were prepared by them dissolving in 37% HCl. 25mg of each samples were digested in 40 ml the HCl and heated to obtain complete dissolution. The volume is made up to 100 ml and 25 ml is taken and made up to 250 ml to obtain 100 ppm (100 mL/g) for the elemental analyses. Fluorine ion concentration is also determined from the solution.
5 Results and discussion

5.1 ISE/ICP-OES results

The amounts of cobalt, lithium and fluoride in each sample are presented in Table 5.1.

Table 5.1 Li, Co, and F content of the prepared samples

<table>
<thead>
<tr>
<th>As-prepared formula</th>
<th>Elemental composition (mole ratio)</th>
<th>x-value</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Co</td>
<td>Li</td>
</tr>
<tr>
<td>LiCoO₂</td>
<td>1.11</td>
<td>1.23</td>
<td>0.88</td>
</tr>
<tr>
<td>LiCo₁.₃₅F₀.₆₅</td>
<td>0.98</td>
<td>1.11</td>
<td>0.85</td>
</tr>
<tr>
<td>LiCo₁.₄₅F₀.₅₅</td>
<td>1.10</td>
<td>1.20</td>
<td>1.03</td>
</tr>
<tr>
<td>LiCo₁.₆₅F₀.₄₅</td>
<td>1.11</td>
<td>1.17</td>
<td>1.16</td>
</tr>
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<td>1.14</td>
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The Co:Li ratio in each compound is approximately 1. This is in agreement with calculated amount used during preparation. The percentage of fluoride in each sample also corresponds to that of the formula.

5.2 TG/DTA data

A thermogram of gel-LiCoO₂ is shown in Figure 5.1 (a). The thermograms of samples with fluorine were difficult to record as samples boiled over the crucible walls, having high amount of organic material (1-butanol and citric acid). TGA from one of the samples, Figure 5.1 (b), for an x value of 0.45, was obtained. It was assumed this thermogram is typical for all the gel samples. The TG analysis was recorded under both oxygen and nitrogen atmosphere. The weight loss in the
range 200 – 300 °C corresponds to loss of water and organic volatiles in the gel. The sharp (fast) loss in weight around 430 °C is the decomposition of nitrate ions and the organic components which serve as fuel. This argument is supported by comparing the slow loss in mass observed under inert (nitrogen) conditions, shown by the dotted thermograms in the figures, that spans the temperature range of 230 and 650 °C for both the LiCoO$_{2-x}$F$_x$ gel samples and the pure LiCoO$_2$ gel sample.

Figure 5.1  TG Thermograms of (a) LiCoO$_2$-gel and (b) LiCoO$_{1.55}$F$_{0.45}$-gel, heating from 30 °C –850°C at 10 °C/min under oxygen (solid) and nitrogen (dotted line) atmosphere

TGA-DTA data for the thermal solid-state samples are shown in Figure 5.2, and for the starting materials for the method in Figure 5.3. From the information obtained there is no suggestion that fluorine has an effect on the thermal behaviour of the sample mixtures for the various values of the fluorine content.
Figure 5.2  Thermograms of solid-state LiCoO$_2$$_x$F$_x$ (0$\leq$x$\leq$0.65): (a) $x=0.65$; (b) $x=0.55$; (c) $x=0.45$; (d) $x=0.35$; (e) $x=0.25$; (f) $x=0.15$; (g) $x=0.08$; (h) $x=0.05$; (i) $x=0$
Figure 5.3 Thermograms of starting materials for the solid-state LiCoO$_{2-x}$F$_x$ compounds: (a) LiOH (b) Co$_3$O$_4$ by the solid-state method.

5.3 SEM micrographs

The SEM micrographs of samples prepared by the sol-gel and solid-state methods are shown in

Figure 5.4 and Figure 5.5 respectively. Among the sol-gel and solid-state synthesized samples of $0 \leq x \leq 0.65$, there seems not to be a significant difference in the morphology of the particles. The samples are dominated by polygonal
particles. Particles of samples synthesized by solid-state show larger sizes and are not as well defined or separated compared to those from the sol-gel method.
Figure 5.4  SEM micrographs of LiCoO$_{2-x}$F$_x$ materials prepared by sol gel: (a) $x = 0$, (b) $x = 0.65$ (c) $x = 0.55$ (d) $x = 0.45$ (e) $x = 0.35$ (f) $x = 0.25$ (g) $x = 0.15$ (h) $x = 0.08$ (i) $x = 0.05$
Figure 5.5  SEM micrographs of LiCoO$_{2-x}$F$_x$ materials by solid-state (a) $x=0$, (b) $x=0.65$ (c) $x=0.55$ (d) $x=0.45$ (e) $x=0.35$ (f) $x=0.25$ (g) $x=0.15$ (h) $x=0.08$ (i) $x=0.05$
5.4 pXRD data

Figure 5.6 (a) shows the pXRD patterns of LiCoO$_{2-x}$F$_x$ ($0 \leq x \leq 0.65$) samples prepared by the sol-gel method. The peaks of each sample with $x$ values of $0 \leq x \leq 0.25$ could be indexed based on $\alpha$-NaFeO$_2$ structure with space group $R\overline{3}m$, indicating single phase in the samples. All peaks (as indicated by asterisks) of samples with $x$ values in the interval $0.25 \leq x \leq 0.65$ could not be indexed to layered structure of $\alpha$-NaFeO$_2$. This is due to the appearance of a secondary phase apart from LiCoO$_2$ in the samples. Purity and crystallinity (ordering of material structure) can be inferred from the pXRD patterns: $I_{(003)}/I_{(104)}$ intensity ratios; lattice parameter ratios and the degree of (006)/(102) and (108)/(110) peak splitting (Zheng, Wu & Yang, 2011).

Although there is appearance of secondary phase in the range of $x = 0.25$ and 0.65, the patterns still show properties of well layered structures from the clear split of the 006)/(102) and (108)/(110) doublets. All samples show an intensity ratio of $I_{(003)}/I_{(104)}$ greater than $> 1.2$, with the lowest of 1.9 recorded for LiCoO$_{1.92}$F$_{0.08}$ and the highest of 2.84 recorded for LiCoO$_{1.85}$F$_{0.15}$. A value less than 1.2 indicates undesirable cationic mixing, which is known to deteriorate electrochemical performance of a material (He et al, 2007; Liu et al, 2007; Xia, Tang & Lu, 2008). The 003 and 004 peaks of $x = 0$–0.65 in the materials were compared in Fig 6.1 (b) and (c). The largest peak shift to lower 2$\theta$ angle is observe for $x = 0.05$. The shift in peak is due to charge compensation when the smaller Co$^{3+}$ ($r = 0.545\text{Å}$) is reduced to larger Co$^{2+}$ ($r = 0.65\text{Å}$) by fluorine substitution; bringing about alteration of the lattice parameter $a$ (a measure of the Co-Co distance in the basal plane of the hexagonal structure) and volume of the unit cell. At higher fluorine amount, $x = 0.35$ and 0.65, the peaks are shifted to higher 20 angle caused by a
decrease in lattice parameter $c$. This is explained as the effect of substituting larger $\text{O}^{2-} (r = 1.40\text{Å})$ by smaller $\text{F}^- (r = 1.33\text{Å})$ overriding the effect of increasing the atomic radii of reduced $\text{Co}^{2+}$ ions (He et al, 2007). Similar shift is also observed for the 004 peak. These observations in peak shift are due to the substitution of oxygen for fluorine in the crystal structure of these materials.

As noted by Zheng and co-workers, the sol-gel method offers thorough mixing of starting materials at atomic scale which is possible for the fluoride ion to be incorporated into the lattice of the material (Zheng, Wu & Yang, 2013). This is the case when the fluoride source is soluble, in the instance of fluorinating $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_{2-x}\text{F}_x$ with $\text{NH}_4\text{F}$. They reported a limit doping amount of $x \leq 0.1$. In this paper LiF is used as the fluorine source and it is first dissolved in 1-butanol. The pXRD patterns show that the fluoride limit could be up to $x = 0.15$. Peaks that could not be indexed based on the $\alpha$-$\text{NaFeO}_2$ structure start to appear beyond this limit, signalling a possible change from the hexagonal layer structure or the presence of impurities (Yue et al, 2013a).

Figure 5.7 shows the pXRD pattern for samples prepared by the thermal solid-state method. Impurity peaks begin to appear as early at the lowest value $x = 0.05$. Appearances of more and pronounced peaks are observed from $x \leq 0.25$. Though there is appearance of secondary phase, the patterns still show properties of layered structure from the clear split of the 006)/(102) and (108)/(110) doublets. On peak shift, the highest shift to lower $2\theta$ angle is observed at $x = 0.08$ in contrast to $x = 0.05$ for the sol-gel method. At higher fluorine amount, the peaks shifted to higher $2\theta$ angle.
Figure 5.6 (a) XRD pattern of LiCoO$_{2-x}$F$_x$ ($0 \leq x \leq 0.65$) materials prepared by sol-gel; (b) and (c) show the positions of 003 and 004 peaks of each sample.
Figure 5.7. (a) pXRD pattern of LiCoO$_{2-x}$F$_x$ ($0 \leq x \leq 0.65$) materials prepared by a solid-state method; (b) and (c) show the position of 003 and 104 peaks of each sample.

5.5 Raman spectroscopy

Figure 5.8 and Figure 5.9 show the Raman spectra of all samples from the sol-gel and solid-state methods.

Two Raman peaks common to HT-LiCoO$_2$ ($R\bar{3}m$ symmetry) layered rock salt structure are recorded for all samples from both synthesis methods irrespective of the extent of fluorination. This demonstrates that the integrity (symmetry) of the layered structure is maintained even at high fluorine content. Though secondary phases are reported from pXRD for materials with high fluorine amount, two
explanations are possible. First is that the layered structure is maintained all through, and the second could be that the secondary phases are not picked up by the Raman measurements.

The Raman peaks were observed at 456-475 cm\(^{-1}\) and 573-589 cm\(^{-1}\) for the A\(_{1g}\) and E\(_{g}\) modes respectively for all samples.
Figure 5.8  Raman spectra of LiCoO$_{2-x}$F$_x$ ($0 \leq x \leq 0.65$): (a) $x = 0.65$; (b) $x = 0.55$; (c) $x = 0.45$; (d) $x = 0.35$; (e) $x = 0.25$; (f) $x = 0.15$; (g) $x = 0.08$; (h) $x = 0.05$; (i) $x = 0.0$; (b) materials prepared by the sol-gel method.
Figure 5.9  Raman spectra of LiCoO$_2$$_x$F$_x$ (0 ≤ $x$ ≤ 0.65): (a) $x$ = 0.65; (b) $x$ = 0.55; (c) $x$ = 0.45; (d) $x$ = 0.35; (e) $x$ = 0.25; (f) $x$ = 0.15; (g) $x$ = 0.08; (h) $x$ = 0.05; (i) $x$ = 0.0; (b) materials prepared by the solid-state method.

As shown from figure 6.5, the peak positions do not match those widely reported in the literature, which are at ca 595 cm$^{-1}$ ($A_{1g}$) and 484 cm$^{-1}$ ($E_g$) (Itoh et al, 1997; Novák et al, 2000; Kushida & Kuriyama, 2002; Mendoza et al, 2004), but they are within the difference of 81 cm$^{-1}$ allowed from these reference Raman shifts. This difference is accounted for by different environmental conditions (equipment, temperature and atmospheric conditions) during measurement (Lemos, 2004). However, the $A_{1g}$ and $E_g$ compared well with those of commercial sample. The difference in Raman shift and intensity among members of same synthesis group were not considered against the fluorine content.
Figure 5.10  Raman spectra of materials prepared by (a) the sol-gel and (b) solid-state. (i) Commercial LiCoO$_2$, (ii) Prepared LiCoO$_2$, and (iii) LiCoO$_{1.55}$F$_{0.45}$

5.6 Identification of the secondary phase

The thought arose that the secondary phase may well be the pure oxydifluoride, LiCoOF$_2$. This compound does not have a structure available in the known databases. In order to test the hypothesis both sol-gel and solid-state formulation with this stoichiometry were prepared and XRD patterns recorded.

A crystal index search was undertaken with the TOPAS-6 software (TOPAS-Academic-6), applying the LSI random search algorithm on a RAW power diffraction pattern of the unknown structure compound LiCoOF$_2$, captured with cobalt incident radiation ($\lambda$=1.789 Å). Consideration was given to the fact that unit-cells derived in this manner, could differ in their unit-cell volume and shape from the original LiCoO$_2$ structure, since a defect has in effect been introduced with fluorine. A single oxygen atom is replaced with two fluorine atoms and the
original point-group symmetry is replaced with an alternative, resulting in a different group symmetry for the solid-state structure. A unit-cell transformation is also likely as a result, with the space group probably reduced to lower symmetry ($C2$ and $P\bar{1}$, Table 5.2) for LiCoOF$_2$. Both instances would require a fresh definition for a new unit-cell origin for the LiCoOF$_2$ structure.

The first cell indexing attempt, following by a full XRD pattern refinement, showed a partially converted LiCoOF$_2$ for the samples ASS to BSG (Table 5.2). The remaining peaks represent a portion of LiCoO$_2$ still being present (Figure 5.11).

A subsequent gel-method preparation of LiCoOF$_2$ revealed an almost fully converted system from LiCoO$_2$ (XRD pattern in Figure 5.12 refers). This unit-cell
volume of 85.62 Å³ and space group ($P\bar{1}$) resembles a logical substitute for LiCoOF$_2$ (retaining a centre of symmetry) derived from LiCoO$_2$ ($R\bar{3}m$) with a volume of 95.27Å³.

![Figure 5.12](image)

**Figure 5.12** X-ray diffraction pattern for almost fully transformed LiCoOF$_2$. The blue pattern represents the RAW unknown LiCoOF$_2$ diffraction profile. The RED pattern represents a whole-pattern refinement of the unit-cell + space group ($P\bar{1}$) Ref. Table-2

These unit-cell and spacegroup indentifications, now offer the possibility of a full structure resolution to be undertaken in the most likely space group symmetry ($P\bar{1}$) and its associated unit-cell dimensions. A final atomic adjustment may then be made by selectively interchanging oxygen for fluorine to converge into a finite structure, to yield the optimum positions for the two fluorine and one oxygen atom positions in LiCoOF$_2$.

Table 5.2 TOPAS whole X-ray pattern refinement parameters (LSI Indexed: unit-cell space group) applied to the five different X-ray diffraction patterns, all captured under Co-
incident radiation. Note the oblique $\beta$-angle, with the b-axis to remain a standard setting for a monoclinic lattice. Refinement detail for one “purely converted” and four “partially converted” samples are shown.

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<th>&quot;Pure&quot; LiCoOF$_2$ X-ray Pattern</th>
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The group of reflections and assigned indices derived from a whole-pattern refinement of the two possible unit-cells (C2 and $\overline{P}$1) are listed in Table 5.3.

Table 5.3 Diffraction peaks and derived indices, with their 2θ positions used in the whole-pattern unit-cell refinements for unknown LiCoOF$_2$, are presented here.

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<td>111.83</td>
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<td>116.42</td>
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<td>1.05</td>
<td>116.41</td>
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</table>
6 Conclusions and recommendation

LiCoO₂ electrode materials were synthesised via two common methods namely the sol-gel and the thermal solid-state methods. As expected the morphology of powder from the sol-gel indicate one that can confer a superior electrochemical properties compare to the thermal solid-state power. This conclusion is drawn from the nano-sized particles and the distribution from the sol-gel method.

In line with the aim of this project to fluorinate LiCoO₂ and to determine the extent to which fluorine can be incorporated into the lattice of LiCoO₂, the following are evident from the pXRD results:

- Flourine was successfully incorporated into the crystal stucture of the materials from the analysis of the relevant peak positions.
- The extent to which the materials can be fluorinated was determine for the sol-gel and thermal solid-state methods.
- More fluorine can be incorporated by the sol-gel method from the delayed in appearance of impurity peaks in the pXRD pattern. The dissolution of LiF in 1-butanol may have contributed to this.
- At the highest amount of fluorine employed in this study, the rhombohedral structure of the compounds was still maintained from the RAMAN spectroscopy.
- In addition, a secondary phase was identified.
- The secondary phase is postulated to be oxydifluoride, LiCoOF₂.
- To determine the structure of LiCoOF₂, crystal index was undertaken and C2 or P\bar{1} were arrived at as the possible space groups.
• From the DTA analyses, crystalisation of LiCoO$_2$ in the sol-gel and solid-state occur at different temperatures. It occurred earlier and at lower temperature in the sol-gel method.

It is recommended that other derivatives of the layered LiCoO$_2$, and spinel structure LiM$_2$O$_4$ be studied, with the same preparation methods. More analytical tools could be employed such as FTIR, XPS and electrochemical testing of the prepared materials, which were not undertaken in this study.
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Appendices

A. X-Ray Diffraction (XRD)

The X-ray powder diffraction technique is an analytical method used to characterize structures. It serves a finger print for characterising unknown crystal structures.

In X-ray diffraction experiment, X-ray are generated by bombardment of materials by beam of energetic electrons (accelerated at high speed through high voltage). The X-ray generator contains a cathode that is heated to generate the electron beam; the beam is then accelerated by a potential difference of approximately 30 kV towards the metal fixed to the anode. The anode material is usually a tungsten filament and anode made of Cr, Fe, Cu, Mo and Ag. The incident electrons ionises some of the metal 1s (K shell) electrons and knocks them off. The vacant 1s level is occupied by an electron from the outer shell L (2p or 3p orbital). The transition from 2p→1s is referred to as Kα and the 3p→1s, Kβ. The Kα transition occurs much more frequently and intensely than the Kβ transition, hence its use in diffraction experiments. The wavelength of the X-ray generated, is characteristics of the of the anode/target materials.

X-ray generated is a continuous spectrum which has to be filtered to obtain a monochromatic X-rays beam to be used in a diffraction experiments. The reason for such filter is to separate the undesired Kβ from the Kα radiation. Filters whose energy of ionization of its 1s electrons (absorption edge) lies between Kα and Kβ is preferred. In such case, the 1s electrons of the filter are ionized by Kβ, absorbing the Kβ and leaving a monochromatic Kα radiation.
Crystal structures are simplified as layers of atoms. These planes are separated by the \( d \)-spacing. When an X-ray beam is incident on crystal materials, the beam interacts with the electrons of atoms on these planes and are reflected. A diffraction pattern is obtained when a constructive interference of the reflected x-ray from different planes is obtained (Figure A1). This occurs when the Bragg’s conditions are met given by the equation:

\[
 n\lambda = 2ds\sin\theta \tag{A1}
\]

where \( \lambda \) = wavelength of incident X-ray, \( d \) = inter-planar distance, \( \theta \) = incident angle between the plane the incident x-ray beam, \( n \) = an integer.

The diffracted beam from the sample planes is detected by either a photographic film surrounding the sample (Debye-Scherrer and Guinier focusing methods) or by using a movable detector, such as Geiger counter, connected to a chart recorder (diffractometer). Data of intensity as function of \( 2\theta \) is obtained.
B. Scanning Electron Microscopy (SEM)

SEM is used to probe external morphology (texture), chemical composition, and crystalline structure and orientation of a specimen. It does this by focusing high-energy electrons onto the surface of the specimen. This generates signals from secondary electrons (backscattered electrons, Auger electrons, characteristic X-rays and cathodoluminescence) which results from the interaction of the primary electron with the specimen. The secondary electrons from which the topography of the surface of the specimen is constructed, is generated by the ionisation of specimen atoms and the emission of loosely bound electrons. Unlike most of the radiation, the secondary electrons are generated close to the surface of the specimen (Figure B1)
Electrons could either be generated by thermionic emission (by heated metal e.g Tungsten) or by field emission guns (by using a strong electric field to extract electrons).

The major components of SEM(Figure B2) are:

- **Electron column**: consists of an electron gun, two or more electromagnetic lenses. The electron guns generate free electrons and are accelerated to
energies in the range 1-40 keV and the lenses create a small, focused, defined electron to form a small focused electron spot on the specimen. This is important to obtain a final high resolution image.

- **Scanning system:** Consists of a scanning coil which scans the electron probe.
- **Detector:** Responsible for collecting and detecting the various signals especially the secondary electron resulting from the interaction of primary electrons with the atoms of the specimen. The detector multiples the secondary electron signal in a repeating process up to 10–20 times large enough to be used to form the image for display.
- **Vacuum system:** A vacuum enables the electron to travel without being scattered. Several types of vacuum pumps are employed to achieve a vacuum environment.
- **Electronic controls:** Controls parameters for resolution (image quality) of final image. Parameters that are control includes electron beam energy, lenses current, aperture size, working distance (WD), and chromatic and achromatic aberration of electron lenses.
- **Display unit:** Monitors the images of the specimen in real time displayed on TV screen or computer monitor.

The samples that were scanned in this work were coated with thin film of carbon by sputtering, to improve their conductivity for good scanning.
Figure B2 Components of SEM
C. F' Ion Selective Electrode (ISE)

Mettler Toledo® pH/ion meter S220 from Mettler Toledo was used to determine selectively, the fluoride ion content in the sample solution.

The technique is potentiometric where potential (voltage) of electrochemical cell is measured. The relation between the electrode potential \( E \) and the concentration of the electro-active component \( A \) is described by the Nernst-equation:

\[
E = E_0 + \frac{2.303RT}{nF} \log(A)
\]  

(C1)

where \( E_0 \) is the standard electrode potential, \( R \) is the universal gas constant, \( T \) is the absolute temperature, \( n \) is the number of moles of electrons transferred in the cell reaction or half reaction, \( F \) is the Faraday-constant, and \( A \) activity of the measured ion.

The complete potentiometric cell consists of a reference electrode and the selective electrode or sensor (Figure C1). The reference electrode houses silver/silver chloride (Ag/AgCl) within a PEI/epoxy body with a potassium nitrate/potassium electrolyte. The selective F' electrode consists of lanthanum fluoride (LaF\(_3\)) crystal electrode doped with europium fluoride (EuF\(_2\)). The inner surface of the crystal is in contact with the inner reference solution of NaF and NaCl, and the outer surface of the crystal is in contact with the solution containing the analyte. The potential that is developed on each side of the membrane is related to the concentration of fluoride in the analytes. This is true since the fluoride ion concentration of the internal solution is fixed.
A standard fluoride ion solutions are used to obtain a calibration plot of mV vs log of concentration where the concentrations of the fluoride of samples are obtained.

Total ionic strength adjustment buffer (TISAB) is use to keep the pH and activity coefficient constant for accurate determination of the fluoride ions.

![Diagram A: Silver wire, Silver chloride salt on silver wire, Ceramic, quartz, or glass fiber junction](image1.png)

![Diagram B: Lead wire, Internal reference electrode (Ag/AgCl), Internal reference solution (containing NaF and NaCl), Single crystal membrane (LaF3)](image2.png)

Figure C1 Basic structure of reference and F ion selective electrodes

D. Inductively Coupled Plasma Optical Emission spectrometry (ICP-OES)

Elemental content in prepared samples were measured with ICP-OES from SPECTRO Analytical Instruments GmbH.
ICP is based on the principle that excited atoms and ions produce electro-magnetic radiations at wavelengths characteristic of each particular element as they relax to their low energy state. The emitted radiation is proportional to the amount of element present and the quantity of the element is determined.

A typical ICP-OES has the following components:

- Sample introduction system (nebulizer)
- ICP torch
- High frequency generator
- Transfer optics and spectrometer
- Computer interface

The nebulizer helps to create an aerosol of very fine mist of sample droplets prior to injection into the ICP. In the ICP torch, the aerosol is desolvated, vaporized and atomized. The plasma excites and ionizes the elemental species in order for the atoms and ions to emit their characteristic radiation.

The plasma is generated from the ICP torch which consists of concentric quartz tubes. The inner tube carries the sample aerosol and Ar support gas and the outer tube contains a flow of Ar gas to cool the tubes (see Figure D1). The inductive coil, connected to a radio frequency generator, sets up an electric field inside the quartz tube. The electrical field induces an azimuthal oscillating current inside the plasma gas, well above the ionisation temperature of the gas, of the order of 10000 to 12000 K.

The light emitted by atoms of elements entrained in the ICP torch is focused by lenses onto a diffraction grating where it is separated into its component
wavelengths in the optical spectrometer. After the light is separated into its different wavelengths (colors), the light intensity is converted to an electrical signal by the photomultiplier tube or semiconductor photo-detectors, and measured. The intensity of a wavelength is compared to previous measured intensities of known concentrations of the element, and a concentration is computed.

**Figure D1 ICP generation**

**E. Raman spectroscopy**

Raman spectroscopy is used for observing vibrationa in a system. The Raman system typically consists of four major components:

- Excitation source (laser).
- Sample illumination system and light collection optics.
- Wavelength selector (filter)
- Detector (photodiode array, CCD or PMT).

In Raman measurements, the inelastic (Raman) scattering is measured and the elastic (Rayleigh) scattering is filtered out. In Rayleigh scattering, the frequency of the photon is the same with that of the scattered laser photons after interaction with the molecule, whereas in the Raman scattering the photon frequency is either shifted up (Stoke) or down (anti-stoke). Figure F1 provides a description of the Raman (Stoke and Anti-Stokes types); and Rayleigh scattering observed when a laser interacts with molecules.

![Raman transition diagram](image)

**Figure F1 Raman transition**

Laser wavelengths ranging from ultra-violet through visible to near infra-red are used in Raman measurements. When laser light interacts with molecular vibration
or phonons, the energy of the incident laser light is either shifted up or down, terms referring to wavelength change.

The Raman effect occurs when photons interact with the polarizable electron density and the bonds of the molecules. For a molecule to exhibit Raman effect, there must be a change in molecular electric dipole-electric polarizability with respect to the vibrational coordinate corresponding to the rovibronic (rotational, vibrational and electronic) state. In this interaction, there is transfer of energy and momentum from the photons to the molecules which accounts for the difference in the energy between the incident photons and the scattered photons. The difference is equal to the difference in the energy between the initial and final rovibronic states of the molecule. Raman shifts are reported in wavenumbers (an inverse value in cm$^{-1}$) which is directly related to energy.