INTRODUCTION
CHAPTER - I

INTRODUCTION

Today’s society needs energy in different forms. Rechargeable batteries are therefore becoming immensely important by virtue of their ability to store electricity and make energy mobile. For many years, the Nickel-Cadmium (Ni-Cd) was the only suitable battery for portable applications such as wireless communications and mobile computing. In 1990, the Nickel-Metal Hydride (Ni-MH) and Lithium-ion (Li-ion) emerged, offering higher capacities.

Li-ion is a low maintenance battery, there is no memory and no scheduled cycling is required to prolong the battery’s life. In addition to high energy density and lightweight, the self-discharge is less than half compared to the Ni-Cd and Ni-MH, making the Li-ion well suited for modern fuel gauge applications. Lithium batteries fulfill many of the demands made in the areas of portable electronics and electrical vehicles to offer high capacities [1].

1.1. HISTORICAL DEVELOPMENT

Lithium is the lightest of all metals, has the greatest electrochemical potential and provides the largest energy content. Pioneering work for the lithium battery began in 1912 by G. N. Lewis but it was not known until the early 1970’s when the first non-rechargeable lithium batteries became commercially available. Attempts to develop
rechargeable lithium batteries were followed in the eighties, in vain. Rechargeable batteries using lithium metal as the negative electrodes (anode) are capable of providing both high voltage and excellent capacity, resulting in an extraordinary high energy density. Cycling altered the lithium electrode, by reducing its thermal stability and causing potential thermal run-away. If this occurs, the cell temperature quickly approaches melting point of the lithium, resulting in a violent reaction. The instability of lithium metal, especially during charging, forced research in a non-metallic lithium battery using lithium ions. Although slightly lower in energy density than lithium metal, the Li-ion is safe, following precautions during charging and discharging. In 1991, the Sony Corporation commercialized the first Li-ion battery and others followed suit. Today, the Li-ion is the fastest growing and most promising battery.

1.2. LITHIUM BATTERIES

Alkali and alkaline earth group metals show high voltages but they react with water. In order to avoid this, non-aqueous solvents are used in place of aqueous solutions. Li, Na, K, Ca and other metals can be used to fabricate batteries with conventional cathodes like MnO₂, PbO₂, CuO₂ and AgCl. These cells show high voltage, long shelf life and high energy density. These cells show

- Long shelf life
- Wide range of operating temperatures
- Low atomic weight
- Good conductivity
1.2.1 Why lithium

Among the various metals, lithium is a promising material because of the following features:

- Low weight (atomic weight 6.94)
- No passivation in non-aqueous solvents like propylene carbonate and ethylene carbonate.
- Wide range of operating temperature
- High specific energy

1.2.2 Advantages of lithium batteries over conventional batteries

A lithium battery system has more advantages than Nickel-cadmium lead-acid and other batteries. Some advantages are as follows:

- **High Voltage**
  Lithium batteries produce more than 3V due to its more electronegative nature and also a very negative standard potential (-3.01V at 25°C)

- **High energy density**
  Lithium batteries are high voltage batteries than conventional Nickel-cadmium or Nickel-Metal Hydride batteries.

- **No memory effects**
  Li-ion batteries have no memory effect as seen in rechargeable Nickel cadmium batteries.
- Dendrite growth
  Lithium-ion batteries have no dendrite growth at anode as seen in other batteries.

- Longer cycle life
  The cycle life is more than 500 times. Repeated use over a long period is possible.

- Minimum Self discharge
  There is no chemical reaction between the electrodes with the electrolyte giving minimum self-discharge.

1.3. CLASSIFICATION OF LITHIUM BATTERIES

The compatible lithium cathodes are selected based on the application of hard sphere model, optimization of critical composition of metal oxides, volumetric capacity and their geometric stability [2]. Electrolytes with high stability, conductivity, compatibility and low viscosity are chosen both as non-aqueous medium and as solid polymeric form. Using a non-oven polymeric separator, cells of different configurations can be assembled as per requirement keeping the above prime factors as key points, Li-batteries can be broadly classified as shown in Fig.1.1.

1.3.1. Primary batteries

These cannot be recharged and so have to be discarded when the cell has delivered all its electrical energy. Many primary cells, in which the electrolyte is an absorbent or separator material (there is no free or liquid electrolyte), are termed as dry cells.
Lithium Batteries

Primary batteries (Non-rechargeable)

Secondary batteries (Rechargeable)

Oxides Sulphides Halides Oxyhalides

Lithiated transition metal oxide cathodes

Rechargeable Lithium Batteries
Anode: Lithium foil
Cathode: Transition metal oxide
Electrolyte: Non-aqueous

Li-ion Batteries
Anode: Carbon
Cathode: Transition metal oxide
Electrolyte: Non-aqueous

Li-Polymer Batteries
Anode: Lithium foil
Cathode: Transition metal oxide
Electrolyte: Solid polymer

Li-ion Polymer Batteries
Anode: Carbon
Cathode: Transition metal oxide
Electrolyte: Solid polymer

Fig. 1.1 Classification of lithium batteries
Applications:

Primary batteries are used for
- Portable electronic devices
- Photographic equipments
- Toys
- Memory back up
- Military applications
- Signaling
- Standby power etc.

Limitations:

The limitations of primary batteries are
- Low energy density
- Poor performance at low temperature
- Evolution of gases on discharge

1.3.2 Secondary batteries

These can be recharged electrically after discharge to their original condition by passing current through them in the opposite direction to that of the discharge current. They are storage devices for electrical energy and are also known as Storage batteries or accumulators.

Advantages:

The main advantages of the secondary batteries are
1. High power density
2. High discharge rate
3. Flat discharge curve and good low temperature performance
Applications:

The applications of secondary batteries are fall into two main categories

➢ Those applications in which the secondary battery is used as an energy storage

➢ Device, generally being electrically connected to and charged by a prime energy source and delivering its energy to the load on demand. Examples are automotive and aircraft systems.

➢ Those applications in which the secondary battery is used or discharged essentially as a primary battery, but recharged after use rather than being discarded. Secondary batteries are used in this manner in electric vehicles for cost savings and in applications requiring power drains beyond the capability of primary batteries.

Limitations:

The limitations of secondary batteries are

1. Relatively low cycle life
2. Low energy density & self discharge as Ni-Fe system
3. Hydrogen evolution
4. High cost

1.3.3. Classification of lithium secondary batteries

The idea of a rechargeable /secondary lithium battery is based on Li insertion reaction. There are mainly three kinds of rechargeable lithium batteries, which are discussed under following sections.
1) Lithium polymer battery
2) Lithium-ion battery
3) Lithium-ion polymer battery

(i) Lithium polymer battery

The development of new type of lithium batteries with thin layer laminated structure is due to the discovery and characterization of ionically conducting polymer membrane. In this, polymeric ion membrane is the key component as it acts both as electrolyte and separator.

In these batteries, the anode material is metallic lithium, cathode material is Li$^+$ insertion electrode and electrolyte used is solid polymer. The reversibility in the positive electrode is due to the use of an insertion electrode material. The positive electrode is a solid, which can incorporate the electroactive material into a solid solution (Fig.1.2) with a wide stoichiometry range as in the following reaction.

**Discharge**

$$\delta \text{Li} + \delta \text{e}^- + \text{Li}_x\text{MO}_2 \rightarrow \text{Li}_{\delta+4} \text{MO}_2 \quad (\text{where } M = \text{Co, Mn, Ni})$$

**Charge**

The electrode undergoes a reversible topotactic redox reaction i.e., the electrode material acts as a host structure, which accommodates guest ions without distortion of the lattice. In these type of batteries, repeated charge and discharge cycle can cause a build-up of surface irregularities (dendrite growth) on the Li electrode to
Fig. 1.2 Lithium polymer battery
such an extend that they penetrate the separator battery positive and negative electrode which creates an internal short-circuit. To reduce such problems, the Li-ion polymer battery emerged.

(ii) Lithium-ion batteries

It is the combination of negative Li⁺ insertion electrode material with another Li⁺ insertion material having a more positive redox potential. In this battery one electrode material releases Li⁺ ions, while the other inserts the Li⁺ ions. The electrolyte may be Li salt dissolved in a mixture of non-aqueous organic electrolyte. This was named as "Rocking chair batteries" (Fig. 1.3). They are otherwise called as “swing”, “shuttle cock” and Li-ion cells.

(iii) Lithium-ion polymer batteries

It is the newest rechargeable energy technology and chemistry to become available for consumer use in portable computers, personal digital assistants (PDA’s) and cellular telephone. It has high voltage per cell (3.8 V average). Here the anode material is carbon, the cathode material is Li⁺ insertion material and the electrolyte is a solid polymer electrolyte results in insertion and de-insertion Li⁺ between the two electrodes at the same time. Thus, it combines the safety aspects of lithium polymer system with the potential energy density of lithium - ion cell. In the polymer battery, the electrolyte is immobilized in the polymer matrix and there is no free liquid in the cell. The polymer systems can be fabricated in very thin formats and packaged in light weight, foil-lined polymer packages. The cells can be combined into series and parallel
Fig. 1.3 Lithium-ion battery
strings to meet most power requirements. Bell core (Bell Communications Research) introduced in 1992 the use of carbon as negative electrode and solid polymer electrolyte. Its merits include slim in thickness, light weight, design flexibility etc.

1.3.4. Advantages of Lithium-ion polymer batteries

a. High energy density

Energy density is an important parameter that determines the size and mass of cell or battery. As portable electronic devices become smaller and lighter and as their functionality increases. A major benefit of Li-ion polymer technology is that it is able to provide the high energy density in the battery. Li-ion polymer cells are thus able to provide an energy density of 160-170 Wh/kg.

b. High voltage per cell

Li-ion polymer cells have an average operating voltage of 3.6V to 3.8V as Li-ion cells. This is three times greater than the operating voltage of both Ni/Cd and Ni/MH. Reducing the number of cells in the battery pack has the benefit of increased reliability and lower assembly costs, since the cell stack is simpler to construct.

c. Excellent cycle life

The cycle life of a rechargeable battery is measured by the number of times it can successfully be charged and discharged. Li-ion polymer cells and batteries have
excellent cycle life. Li-ion polymer batteries or cells do not have catastrophic cycle life failure.

d. High charge efficiency

Li-ion polymer cells are almost perfectly charge efficient. This means that the number of Ah required to charge a Li-ion polymer cell is > 99.8% of the Ah delivered on the subsequent discharge. This high charge efficiency allows charges to be small in size without wastage.

e. Low self-discharge

Self-discharge is the electrical capacitance lost during long time storage. Self-discharge is caused by electrochemical processes within the cell and is equivalent to the apply of a small external load. Li-ion polymer cells typically lost 8% of their capacity for the first month and then 2% for each subsequent month. Thus, in order to reduce self-discharge, it is recommended to store Li-ion polymer cells at lower temperatures. Ni/Cd and Ni/MH cells suffer self-discharge rates as high as 25% per month.

f. Low temperature operation

Li-ion polymer cells are capable of delivering good capacity at low temperature (-20°C), although the capacity delivered is much less than that delivered at room temperature, the fact that the use of portable electronic equipment at low temperature is often limited in time, means that the user is still able to power the devices.
g. Flexible designs

Li-ion polymer cell uses a ‘stocked’ construction, adjusting the electrode/electrolyte structure, is easy and cost effective. In this way, Li-ion polymer cells exhibit flexibility in their mechanical properties and in their design and construction.

h. Attractive thin and flat form

Li-ion polymer batteries employ a thin (110 μm), polymer - based packaging material to contain the electro chemical materials. This allows the system to have a flat and moreover thin (2 to 5 mm) form factor.

i. Excellent safety features

Li-ion polymer cells do not use metallic lithium (or) Li-alloys and lithium is used only in the ionic form and this greatly improves the safety of the Li-ion battery.

j. Environmental friendly

Li-ion polymer cells are environmental friendly, as they do not contain toxic metals.

1.3.5. Applications of Lithium-ion polymer batteries

1. Li-ion polymer batteries possess a wide range of applications in light weight, short and small products.

2. Associated application products include Laptop, MD players, handy recorders, note book personal computers, cellular phones, digital still cameras and wireless earphone etc.
LITHIUM-ION BATTERIES APPLICATIONS
1.4. MATERIALS DEVELOPMENT FOR RECHARGEABLE Li-BATTERIES

1.4.1. Anode Materials

1.4.1.1. Lithium Metal

The highest electrochemical reduction potential of lithium (-3.045 V) makes it a potential negative electrode in rechargeable lithium batteries. Lithium is the lightest of all metals with an atomic mass of 6.94. It has a specific capacity of 3.86 Ahg\(^{-1}\) which is three times that of sodium (1.165Ahg\(^{-1}\)). It is easy to fabricate lithium as thin sheets or foils and is less prone to bulk oxidation because a semi-protective film forms on its surface in air. Lithium is easily attacked by moisture when in finely divided form, ignites spontaneously in contact with water and reacts with oxygen and nitrogen in humid air. Lithium is hence handled in dry rooms or glove boxes constructed specially for lithium battery work. Comparison of Li negative electrode with Cd & Zn is shown in Table 1.1. The drawback associated with it is the inability to cycle lithium electrode with high efficiency over long period of time.

Dendrite growth

Dendrite formation on lithium electrode causes capacity losses by redistributing lithium from the bulk to the isolated islands as shown in Fig.1.4. This problem arises due to the high solubility of the discharge product in the alkaline electrolyte [3]. During discharge, a proton of the discharge product dissolves and re-deposits back on the electrode structure on charging. Due to a number of effects (thermal concentration
### Table 1.1

Comparison of lithium negative electrode with Cd and Zn

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Lithium</th>
<th>Cadmium</th>
<th>Zinc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity (Ah cm⁻³)</td>
<td>2.05</td>
<td>4.13</td>
<td>5.85</td>
</tr>
<tr>
<td>Specific capacity (A hg⁻¹)</td>
<td>3.86</td>
<td>0.48</td>
<td>0.82</td>
</tr>
<tr>
<td>Standard potential (V)</td>
<td>-3.04</td>
<td>-0.40</td>
<td>-0.76</td>
</tr>
<tr>
<td>Specific Energy (Wh g⁻¹)</td>
<td>11.7</td>
<td>0.19</td>
<td>0.62</td>
</tr>
</tbody>
</table>
Fig. 1.4 Dendrite formation on a lithium electrode causes capacity loss by redistributing Li⁺ from the bulk to isolated islands in the electrolyte.
gradients and current density distribution), the dissolution and re-deposition process is not mirrored.

During the charging process, the re-deposited lithium can grow into needle like shapes which are called dendrites. These dendrites can pierce the separator material and touch the other electrode active surface resulting in an internal short circuit. This causes premature cell failure.

The above problem does not, however, preclude the use of lithium metal as the negative because the quality of lithium plating reaction depends strongly on the electrolyte composition. Active research is still pursued to find out suitable electrolyte compositions and its compatibility with lithium negative electrodes to overcome the above problems.

1.4.1.2. Lithium alloys

Lithium alloys are used as insertion electrode materials in high temperature cells. These cannot be used at very low temperatures, because of the very low diffusion coefficient of lithium, for example in the α-aluminum phase which forms on discharge of LiAl-alloy. Other alloy negative electrodes proposed include Li-Sn, Li-Sn-Sb, etc. [4] according to the general scheme shown in the equation below:

\[
\begin{align*}
\text{Discharge:} & \quad \text{Li}_x\text{M} & & \rightarrow & & x\text{Li}^+ + xe^- + \text{M} \\
\text{Charge:} & & & & & \\
\end{align*}
\]
1.4.1.3. Carbon

Carbon is used as the negative electrode in commercially rechargeable lithium batteries called as rocking chair batteries which exhibit both higher specific charges and more negative redox potentials than most metal oxides, chalcogenides and polymers. Due to their dimensional stability, they show better cycling performance than lithium alloys. The insertion of lithium into carbon proceeds according to the following equation:

$$\text{Discharge} \quad \text{Li}_x\text{C}_n \rightarrow x\text{Li}^+ + xe^- + \text{C}_n$$

Charge

Carbon capable of reversible lithium intercalation can roughly be classified as graphite and non – graphite (disordered). Mesophase carbons, carbonaceous materials with a layered structure typically with a number of structural defects are also employed as anode materials.

1.4.1.4. Graphite

Although the carbon has several allotropes, graphite is used as practical anode material for Li-ion batteries. Graphite is one of the first known examples of an insertion electrode, with an ability to accept lithium up to a stoichiometry of LiC$_6$, corresponding to a theoretical specific capacity of about 370 Ah kg$^{-1}$. It is a typical layered compound that consists of hexagonal graphene sheets of SP$^2$carbon atoms, weakly bonded together by Vanderwaals forces into an ABAB… stacking sequence along the c-axis as shown in
The lattice belongs to a space group of $P\overline{6}_3/mmc$, and the $a$- and $c$-axis lengths of the hexagonal unit cell are $a_0=0.246\text{nm}$ and $c_0=0.6708\text{nm}$ respectively at room temperature. Graphite crystal has two kinds of characteristic surfaces, normal and parallel to its $c$-axis, which are called the basal phase and edge plane respectively. This anisotropic structure is an important feature that determines the properties of lithium intercalation within graphite. Carbons obtained by pyrolyzing organic precursors such as phenolic and epoxy resins at low temperature can reversibly intercalate Li atoms with capacity greater than that of graphite [5].

1.4.1.5. Nitrides as new anode materials

The lithium-metal-nitrogen ternary system is a new candidate for the reversible anode. The nitride system belongs to the group of compounds having antifluorite [6,7] or Li$_3$N [8,9] structure. Both structures are known to be good ionic conductors, hence high lithium ion mobility and reversibility can be expected for the system. In addition they show a negative potential close to that of lithium metal, indicating that the nitrides may be a good anode candidate.

a) Antifluorite structure

Li-M-N compounds with antifluorite structure, where M stands for a transition metal, have been known for a long time, e.g., Li$_3$TiN$_4$, Li$_7$VN$_6$, Li$_7$CrN$_6$, Li$_7$MnN$_6$, Li$_7$FeN$_2$, etc. Both Li$_3$MnN$_4$ and Li$_7$FeN$_2$ could be easily synthesized using traditional ceramic method by reacting the transition metal nitride M$_x$N$_y$ and lithium nitride Li$_3$N.
Fig. 1.5 Schematic diagram of graphite
in a 1% H₂ - 99% N₂ stream. The crystal structure of Li₇MnN₄ and Li₇FeN₄ by Rietveld refinement using the space group P3n are illustrated in Figure 1.6. Li₇MnN₄ has isolated MnN₄ tetrahedra. The nitrogen atoms are arranged in a distorted cubic close-packed array and the tetrahedral in which Li and Mn atoms are located to form an anionic three-dimensional network. Both Li₇MnN₄ and Li₇FeN₄ have good reversibility and high specific capacities of 150 mAh/g and 210 mAh/g, respectively.

b) Li₃N structure

Another ternary lithium transition metal nitride system, Li₃₋ₓMₓN (M = Co, Ni and Cu), is isostructural to Li₃N, which is composed of Li⁺₂N⁻ layers with Li⁺ between them as described in Figure 1.7. Metal ions, Co, Ni and Cu can be substituted for lithium between the Li₃N layers. The solid solutions region of Li₃₋ₓMₓN prepared under flow of N₂ gas are in the range of 0 ≤ x < 0.5, 0 ≤ x < 0.6 and 0 ≤ x < 0.3 for M = Co, Ni and Cu, respectively. As the M⁺⁺ (especially Co⁺⁺ and Ni⁺⁺) and M⁺ states coexist in Li₃₋ₓMₓN, the same number of lithium defects are created. The system is correctly represented as Li₃₋ₓ(M⁺⁺ₓM⁺)(N) where y indicates number of lithium vacancies. In stoichiometric Li₃₋ₓMₓN, the doped metals exist as M⁺ ion in the structure. When a lithium ion is deintercalated, an M⁺ ion will be oxidized to M⁺⁺. Li/ Li₃₋ₓMₓN cells were cycled in the range of 0 ≤ z ≤ 1.0 and showed a high capacity of 480 mAh/g in Li₂₋₀.₄CoN, and 460 mAh/g in Li₂₋₀.₄CuN, while it is only 200 mAh/g in Li₂₋₀.₄NiN. The high capacity of Li₃₋ₓMₓN is due to the amorphous phase, which shows good reversibility.
Fig. 1.6 The crystal structures of
(a) Li$_7$MnN$_4$ (b) Li$_3$FeN$_2$
Fig. 1.7 The crystal structure of Li$_x$M,N
1.4.2. Cathode materials

Strongly oxidizing intercalation compounds are compounds those reversibly intercalate lithium above 4V. They must be used as the positive active materials. Layered type transition metal oxides such as LiCoO₂, LiNiO₂ and LiMn₂O₄ spinel are the best among the compounds that can reversibly intercalate lithium at such voltages.

1.4.2.1. Transition metal oxides as the most attractive cathode materials for rechargeable lithium batteries

Electron transfer in a solid matrix is easily attained compared to the lithium-ion transfer. The ionic radius of lithium ion is 0.90Å (CN=6) and 0.73 Å (CN=4), which are larger than those of trivalent and tetravalent transition metal ions. Hence, quite opposite conditions for cations in solid matrix are required. i.e., the smaller transition metal ions at octahedral sites have to be immobile and the larger lithium ions at the octahedral sites have to be mobile. The transition metal ions may be immobile when the covalence between transition metal and oxygen ions to form MeO₆ is strong enough to fix the transition metal ions at octahedral sites. Lithium species surrounded by six or four oxygen ions are believed to be more ionic. Although the ionic radius of lithium ions is too large to move freely in a solid matrix, lithium ions at octahedral sites may move from one site to the other with the aid of lattice vibration and the fluctuation of oxygen ions mainly due to the electrons accepted by neighboring transition metal ions. The necessary condition for the crystal structure of a solid matrix is that all vacant
octahedral sites in MeO$_2$ should be linked with each other forming a one-dimensional tunnel (channel) or two-dimensional triangular lattice space to transport and accommodate lithium ions. Since γMeO$_2$ and LiMeO$_2$ are interchangeable via topotactic reaction, many crystal structures suitable for this purpose can be evaluated. They are called layer, channel, [1x1]-tunnel and [2x2]-tunnel structures, in which it is possible to transport and accommodate lithium ions throughout a solid matrix concurrently with electron transport via the transition metal ions at the octahedral sites.

Thus for topotacticity, specific features with respect to chemical composition, solid geometry of a matrix and the nature of solid-state redox reaction need to be considered. Additional conditions are the availability, economy of the transition metal elements and the ease of synthesis of cathode materials using transition metal compounds. Such conditions lead us to investigate the electrochemistry of 3d-transition metal oxides as the choice of cathode materials for developing rechargeable lithium batteries. The important chemical species for topotacticity are tetravalent and trivalent transition metal ions located at the octahedral sites in the close-packed oxygen array. Many transition metal ions especially in tetravalent and trivalent states show ionic radii between 0.5Å$^+$ and 0.8Å$^+$ suggesting that the tetravalent metal ions can accept electrons and form the trivalent ions at octahedral sites without the destruction of octahedral coordination which is a necessary condition for a solid-state redox reaction of topotactic chemistry.
The size of the transition metal ions at octahedral sites in the close packed oxygen array is one of the key factors in realizing topotactic reaction. When the transition metal ions accept electrons, they usually enlarge at the same position. If the enlargement of ions exceeds a certain elastic limit, the solid matrix will be destroyed entirely. Although the value of elastic limit is not known, one can estimate the value from the available structure data combined with the electrochemical data. When the ratio of transition metal and oxygen ions radii (cation to anion ratio) is in the range 0.41 to 0.71, octahedral co-ordination is preferred in the close packed oxygen array. The ionic radii of transition metal ions to be located at octahedral sites are calculated to be in the range between 0.5Å and 0.9Å using 1.4Å (CN=6) for the oxygen ion. Therefore, transition metal oxides are the obvious choice as electrode material for use in rechargeable lithium batteries.

In lithium batteries, strongly oxidizing compounds i.e. compounds those can reversibly de-intercalate Li around 4V, are used as positive electrodes. Of all the existing cathodes, there are only three outstanding classes of compounds viz., LiMn\textsubscript{2}O\textsubscript{4}, LiCoO\textsubscript{2} and LiNiO\textsubscript{2} that satisfy the aforesaid requirements and offer high voltage, high energy and extended cycle life with high reversibility. The discussion about these three electrodes is as follows:

a) LiCoO\textsubscript{2} and its derivatives

LiCoO\textsubscript{2} is classified under rhombohedral crystal lattice that is iso-structural with the layered α-NaFeO\textsubscript{2}. Its structure is based on a close-packed network of oxygen atoms
with Li⁺ and Co³⁺ ions (occupying the 3a and 3b O₈ sites respectively) ordering an alternate (111) planes of the cubic rock-salt structure. This ordering introduces a slight distortion of the lattice to hexagonal symmetry. Hence LiCoO₂ crystallizes in the space group R-3m with cell constants a=2.816Å and c=14.08Å [10]. A schematic view of the crystal structure in Fig.1.8 shows the ...ABCABC...type stacking of the ...O-Li-O-Co-Li-O... triangular sheets. The theoretical capacity of cobaltate is rather high (274mAh/g), but practically it can yield about 165mAh/g i.e., only 55-65% of the theoretical value. This is due to the fact that when charged to voltages above 4.25V the crystal structure of lithium cobaltate undergoes irreversible changes, leading to deterioration in its electrochemical characteristics. Therefore the admissible voltage range during the cycling of lithium cobaltate cathode is limited between 3 and 4.25V [11]. A lot of work worldwide has also been dedicated to partial substitution of cobalt by other metals like nickel, iron and manganese [12-16]. Substitution with aluminium has shown an increase of the average discharge voltage which has predicted by the theory involving the participation of oxygen ions bonding in the oxidation reduction process [17, 18]. Substitution with magnesium has impact on fading behaviour during cycling [19].

b) LiNiO₂ and its derivatives

The main advantages of LiNiO₂ are the low cost, less toxic, maximum charging voltage higher capacity and better reversibility compared with LiCoO₂ and LiMn₂O₄. LiNiO₂ is iso-structural with LiCoO₂ and crystallites with a rhombohedral layered rock-salt structure, in which Li⁺ and Ni³⁺ ions occupy the O₈ 3a and 3b sites in
Fig. 1.8 ABCABC...type stacking of the ...O-Li-O-Co-Li-O...

triangular sheet arrangement in LiCoO₂.
the FCC packing oxygen lattice. These cations are ordered along the [111] direction of the rock salt cubic lattice, leading to a 2D structure. The cell dimensions of LiNiO₂ are \(a_0=2.88\,\text{Å}, c_0=14.19\,\text{Å}, c_0/a_0=4.9\) in hexagonal settings) very close to the corresponding value of a cubic cell \(a_0=c_0/2\sqrt{3}=4.1\,\text{Å}\) suggesting that the displacement of Ni and Li ions occur easily without a dimensional mismatch compared to that of LiCoO₂. Fig. 1.9 shows the structural models of ideal LiNiO₂ and Li₁₋ₓNiₓO₂ with \(x>1\). The excess nickel is considered to be substituted for lithium defects, and the formula can be expressed as \([\text{Li}_1,\text{Ni}_1]\_3\,\text{[Ni}_1,\text{Li}_1\_3\]O} \_2\) [20,21]. This in turn makes the preparation of battery active LiNiO₂ very difficult. Also Li-Ni-O system is characterized by the existence of LiₙNi₂₋ₓO₂ solid solution, thus making the synthesis of phase-pure LiNiO₂ more difficult.

For lower values of \(x\), Li/Ni mixing (cation mixing) occurs leading to the presence of \(\text{Ni}^{2+}\) within the Li layers, which ultimately is detrimental to the electrochemical performance of the material (lower capacity and high ) [20,22]. This type of cation mixing can be controlled to be a minimum by adopting proper synthesis procedures. Disadvantages of LiNiO₂ also include giving higher fading with cycling. Improvement of reversibility and fading behaviour is also observed by co-substitution of cobalt and manganese of up to 40% of the nickel [23].

c) LiMn₂O₄ and its derivatives

LiMn₂O₄ crystallizes as a cubic spinel structure and can be represented as \(\text{A}[\text{B}_2]\text{X}_4\). The unit cell of the cubic spinel \(\text{A}[\text{B}_2]\text{X}_4\) contains 32 anions in a cubic close
Fig. 1.9 Structural models of
(a) IDEAL LiNiO₂ (b) LiₓNi₁₋ₓO₂ WITH x > 1
packed array (32e positions of the \textit{Fd3m} space group). In the case of LiMn$_2$O$_4$ spinel cathodes, ‘A’ represents lithium cations, ‘B’ the manganese (tri- and tetra-valent) cations and ‘X’ denotes the oxide ions. The cations occupy the 8a tetrahedral (T$_4$) interstices and the B cations occupy the 16d octahedral (O$_6$) interstices. In addition to these occupied sites, empty 16c O$_6$ sites share faces with 8a and 48f T$_4$ sites to provide continuously interconnected 3D polarization interstitial space, through which lithium ions can diffuse \cite{24}. The 8b T$_4$ sites share all four faces with 16c sites occupied by the B cations, so they are inaccessible to inserted lithium. The crystal lattice parameter of LiMn$_2$O$_4$ as determined from XRD is 8.24Å\(^2\). The crystalline structure of LiMn$_2$O$_4$ is given in Fig.1.10.

The presence of cations other than Li\(^+\) in the A sites impedes lithium transport through the interstitial space, thus affecting the electrochemical properties drastically. Li\(^+\) insertion and extraction involves the 16c O$_6$ sites of the spinel structure. Since each 16c sites share two faces with 8a sites, there is an electrostatic repulsion of the A cations into vacant 16c sites. Of the three oxide cathodes, LiMn$_2$O$_4$ is particularly attractive because it is relatively cheap and non-toxic. A discharge capacity of about 130mAh/g has been realized from this compound \cite{25}. Long term electrochemical cycling and storage studies with this oxide in lithium batteries indicate irreversible capacity loss. Improvement of fading and rate of capacity loss are decreased by substitution of elements like iron, cobalt, nickel or more exotic ones like magnesium, titanium, silver and copper \cite{26-30}. 

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Fig. 1.10 LiMn$_2$O$_4$ spinel structure showing the position of various atoms
1.4.3. Electrolytes

Suitable non-aqueous electrolyte for rechargeable lithium cells employing insertion electrodes can be roughly divided into three groups.

(i) Liquid electrolyte
(ii) Solid electrolyte
(iii) Polymer electrolyte

(i) Liquid electrolyte

In lithium-ion rechargeable battery, aqueous electrolyte cannot be used as it would undergo decomposition. Hence an organic liquid containing dissolved inorganic salts (e.g. LiClO₄, LiPF₆, LiAsF₆ etc), with a large stability window has been considered as an electrolyte. A typical liquid electrolyte consists of a Lithium salt Li⁺ X⁻ dissolved in an aprotic organic solvent or a mixture of aprotic solvents. e.g. esters and ethers. The solvent should be essentially aprotic, as active protons react with lithium to give hydrogen gas. For example, the use of acids and alcohols are prohibited.

\[
2\text{ROH} + 2\text{Li} \rightarrow 2\text{ROLi} + \text{H}_2
\]

Electrolyte salts

These are salts that provide solutions of reasonable conductivity in a suitable organic aprotic solvent e.g. LiAlCl₄, LiBF₄, LiPF₆ and LiAsF₆. LiClO₄ is not recommended for battery application due to the explosive hazard in an organic solvent.

Aprotic solvents

Some of the aprotic solvents are given below:

a) Cyclic esters: Ethylene carbonate(EC), Propylene Carbonate(PC).
γ -Butyro - lactone(BL)

b) Linear esters: Methyl formate, Methyl acetate and Diethyl carbonate

c) Cyclic ethers: Dioxalane (DIOX), Acetonitrile (AN), Tetrahydrofuran (THF), Dimethyl Sulfoxide (DMSO).

The ionic conductivity of Li-ion is proportional to its mobility and the number of Li-ion. Although cyclic carbonic acid esters (carbonates) like PC and EC have high dielectric constant, their viscosity values are high, especially, due to the interaction between the molecules, which results in deviation of electric charge of the molecule. Lower viscosity is more desirable for easier movement of Li-ion. On the other hand, in chain-like esters like dimethyl carbonate (DMC) and diethyl carbonate (DEC), even though their viscosity and dielectric constant values are considerably low, they do not remain much restrictions for the movement of Li-ions between the molecules. If the dielectric constant becomes large, the coulombic force between positive and negative sites in a molecule will become high, imparting fair degree of ionic dissociation in the neighboring molecules. It is common to mix and use two or more solvents so as to obtain resultant property, which suits to provide high performance battery.

(ii) Solid electrolyte

In true solid electrolyte only Li⁺ ions are mobile. The transference number of Li⁺ is one. Other (much less mobile) ions in a solid electrolyte are arranged in a crystalline or glassy matrix in which Li⁺ moves through vacant and / or interstitial sites. This type of Li⁺ transport occurs in inorganic solid electrolyte. At ambient temperatures, the
ionic conductivity of solid electrolyte is poor. Thus, only very thin electrolyte films can be used.

(iii) Polymer electrolyte

A liquid electrolyte must be in a porous solid or elastomeric separator to prevent direct contact between the electrodes. A stack pressure is generally applied to ensure good inter particle contact with in the electrode material while dimensional changes in the electrode particles occur during cycling problems arise because separators containing liquid electrolyte tend to dry out. This is particularly so with gas evolution during the first cycle. Containment of the liquid electrolyte in a separator can cause problems due to non-uniformity in the stack pressure and the current path.

The advantages of polymer electrolyte are their higher mechanical stability and flexibility which allow simple fabrications of electrolyte films.

1.4.4. Separators

Separators must be electronically insulating membranes that permit ion transport across them. They must be thin, mechanically strong and must be sufficiently porous to accommodate electrolyte solution in their matrix. Typical separators used in Lithium batteries are poly ethylene-poly propylene membranes with more than 35% porosity.

1.5. STIMULATION FOR THIN FILM PREPARATION

Compared with LiMn$_2$O$_4$ powder, the capacity loss of LiMn$_2$O$_3$ thin film is very small. It shows very good cycling behaviour. This is caused by two factors [32]. The first
is that the grain size of thin film is much smaller than the powder, these small grains greatly increase the effective surface area of electrode, to make the intercalation and deintercalation of lithium ion into and out of LiMn$_2$O$_4$ much easier, to give good cycling behaviour. The second is that the thickness of thin film is very small, i.e., the diffusion route of lithium ion inside the thin-film electrode is very short, avoiding the cathode entering Jahn-Teller effect zone during deep discharge. In the discharge process of the intercalation of lithium ion, if the electrode is thick, the lithium concentration at the interfaces near electrolyte and current collector will be different. This is due to the small diffusion rate of lithium ion inside the electrode. In this case, the surface of the electrode has been already in the Jahn-Teller effect zone, results in bad cycling behaviour. While for the thin-film electrode, the electrode is very thin, which can greatly decrease the lithium concentration difference throughout the electrode entering the Jahn-Teller effect zone during deep discharge, leading to good cycling behaviour. Since the nano-size particle is prepared in thin film form has more cyclic behaviour and specific capacity. So microemulsion method gives a nano level particle. This particle is coated in substrate to form thin film.

1.6. THIN FILMS MATERIALS AND ITS APPLICATIONS

A material having one of its dimensions about one micron (or) less is the geometrical description of “thin film”. Thin films have very large surface-to-volume ratio and consequently the surface usually influences the properties of the film greatly. Because of compactness, better performance and reliability coupled with the low cost of
production and low weight, thin film devices are preferred over their bulk counterparts [32]. Packing more power into batteries while reducing their size and weight has become a goal for researchers because of growing interest in smaller, lighter batteries for a variety of purposes. Battery cell components can be prepared as thin sheets built up as layers. The area and thickness of the sheets determine battery capacity. Thin films increase the contact area of the cell components, resulting in a high fraction of reactants. Thin films result in higher current densities and cell efficiencies because the transport of ions is easier and faster through thin-film layers than in bulk materials.

1.6.1 The solid-state thin-film batteries will offer the following advantages over competitive technologies:

- They are rechargeable.
- They have high power and energy densities.
- They can be fabricated to virtually any size onto a variety of substrate materials, such as semiconductors, ceramics, and plastics.
- They can be fabricated using standard deposition techniques and mild deposition conditions.
- They can operate over a wide temperature range, even at temperatures near the melting point of lithium.
- They contain no liquid components and produce no gases.
- Thickness of thin film is very small. So the diffusion route of lithium ion inside the thin film electrode is very short.
1.7. VARIOUS THIN FILM TECHNIQUES FOR THE PREPARATION OF THIN FILM CATHODE MATERIALS

Physical vapour deposition (PVD) and chemical vapour deposition (CVD) are common methods for transferring material by atom-by-atom from one or more sources to the growth surface of a film being deposited onto a substrate. The deposition is normally carried out in a vacuum chamber to enable to control of the vapour composition. If the vapour is created by physical means without a chemical reaction, the process is classified as PVD. Many deposition methods have been developed in efforts to balance advantages and disadvantages of various strategies based on the requirements of purity, structural quality, the rate of growth, temperature constraints and other factors. The various methods used in the deposition of thin films are given below.

1.7.1 Physical Vapour Deposition (PVD) Methods

There are numerous methods of physical vapour deposition such as thermal evaporation, electron beam evaporation, pulsed laser evaporation and molecular beam epitaxy. The objective of these deposition processes is to transfer atoms from a source to substrate where film formation and growth follow automatically.

1.7.1.1 Thermal evaporation

In this method, thin films are prepared by the condensation of vapours produced by either evaporation or sublimation on to the substrates. The most widely used thermal evaporation is simple and very convenient. Excellent and detailed reviews
of the know-how of thermal evaporation is available [9]. Preparation of thin film by thermal evaporation is carried out in high vacuum to increase the mean free path of vapour atoms/molecules, to avoid contamination and to get uniform films. Thermal evaporation may be achieved directly or indirectly by a variety of physical methods.

1.7.1.2 Electron beam evaporation (EBE)

In electron beam evaporation, an electron beam is accelerated through a potential of 5 to 10 kV and focused on the material. The electrons lose their kinetic energy mostly as heat and the temperature at the focused spot can become as high as 3000°C. At such high temperatures, most of the refractory metals and compounds can be evaporated. Since the temperature is high only at the focused spot, rest of the material would be cool. The result is lesser interaction between the material and the support thereby reducing the contamination. Since the input power can be very high, extremely high rates of evaporation can be achieved even for high melting point materials.

1.7.1.3 Pulsed laser evaporation

Laser is a powerful tool in many applications especially in material processing. It possesses many unique properties such as narrow frequency band width, coherence and high power density. The light beam is intense enough to vaporize the hardest and most heat resistant materials. Besides, due to its high precession, reliability and spatial resolution, it is widely used in the industry to process materials like matching of the thin film, modification of materials, heat treatment, welding and micro patterning. The
enormous intensity of a laser beam may be used to heat and vaporize materials by keeping the laser source outside the vacuum system and focusing the beam on the surface of the material to be evaporated. Using material in powder form can reduce degassing of the specimen.

1.7.1.4 Molecular beam epitaxy (MBE)

The molecular beam epitaxy produces epitaxial films by condensation of atoms. The deposition of single crystal (epitaxial) films are made by the condensation of one or more beams of atoms or molecules from the source under vacuum conditions. The evaporation sources consists of a metallic chamber, containing the evaporant with a small orifice. The orifice dimension is smaller than mean free path of the vapour in the chamber and the flow of molecules from the source is by effusion. The effusing molecular beam is precisely determined by the partial pressure of the vapour species within the chamber, their molecular weight, source temperature and orifice dimension. The beam is directed onto the substrate by the orifice slits and shutters.

1.7.1.5 Sputtering

Sputtering was first discovered in 1852. When a solid or liquid is bombarded with atoms, ions, or molecules, several phenomena may arise, depending on the kinetic energy of the bombarding particles. At very low kinetic energy (<5eV), the interaction is confined to an outermost layer of the target material. Ions of noble atoms may be reflected on coming into thermal equilibrium with the surface and be evaporated. The
potential energy of the species plays an important role because it is responsible for the ejection of secondary electrons or absorbed surface impurities or to the breaking of chemical bond. At kinetic energy which exceeds the binding energy of the atoms, atoms in the lattice are pushed into new position giving rise to surface migration and surface damage. At energies exceeding roughly 4H (H=heat of sublimation of target material) the dislodging of atoms and their ejection to gas phase begins. This process is called physical sputtering. Electron is a clean surface would need much higher kinetic energy (about 500 KeV for Co) to accomplish physical sputtering. For bombardment of surface under normal incidence more than one collision is necessary for the ejection of a sputtered atom because the momentum vector has to be changed by more than 90. Only under oblique bombardment one can detect forward sputtering atom or ions which result from a single collision between an ion and a surface atom.

The ion bombardment of polycrystalline metal target was observed as early as 1912 and the results strongly suggested that the sputtering yield must be sensitive to crystal orientation. In 1955, a rather unexpected phenomenon relating to a single crystal sputtering was discovered that the sputtered atoms are preferentially ejected in the close packed crystal direction.

When a surface of a solid is bombarded with ions, several interactions of the ions with surface may happen.

1. The incident ions are reflected, probably being neutralized in the process.
2. The impact of the ion causes the target to eject a secondary electron.
3. The ion impact causes some structural rearrangements in the target materials.
4. The ion is buried in the target. This is ion implantation.

5. The ion impact sets a series of collisions in the target, possibly leading to the ejection of one of these atoms. Sputtering is the atom-by-atom deposition technique.

Sputtering is predominant in the energy region of incident electrons 100 eV to 100 KeV. At higher energy region, the ion implantation becomes predominant.

1.7.2 Chemical Vapour Deposition (CVD) Methods

Chemical deposition techniques are most important methods for the growth of films owing to their versatility for depositing a very large number of elements and compounds at relatively low temperatures. The processes are very economical and have been industrially exploited to a large scale.

The two important chemical deposition processes are briefly discussed below:

- Chemical vapour deposition
- Spray pyrolysis

1.7.2.1 Chemical vapour deposition

A simple definition of chemical vapour deposition is the condensation of a compound or compounds from the gas phase onto a substrate where reaction occurs to produce a solid deposit. The gaseous compound, the deposit material is formed by volatilization from either a liquid or a solid feed and is caused to flow either by a pressure differential or by the action of carrier gas to the substrate. The chemical reaction is initiated at or near the substrate surface, which produces the desired material
in the form of a deposit on the substrate. The morphology, microstructure and adhesion of the deposit are strongly influenced by the nature of chemical reaction and the activation process.

1.7.2.2. Spray pyrolysis

Spray pyrolysis has been extensively used to deposit thin film oxides on large area substrates. In principle, two types of experimental set ups are used to grow the oxides films using technique (33,34).

a) Conventional set up

b) Set up with preheat treatment

The conventional spray pyrolysis technique consists of spraying a diluted solution of appropriate substances from an atomizer into a heated substrate under normal atmospheric conditions or controlled atmospheres. High pressure argon, nitrogen or air is usually used as spraying gas. The solutions are made by dissolving in suitable solvents such as ethanol, butyl acetate, propanol, hydrochloric acid and water.

In the arrangement with preheat treatments a furnace to preheat, the spray is placed between the atomizer and the substrate. The distance between the substrate and atomizer nozzle may be equal to or larger than about 20 cm and the typical gas flow rates are about 5ml per min. To obtain more homogeneous films either rotating the substrate or rotating the sprayer is used.
1.7.2.2.1. Advantages of spray pyrolysis technique

The chemical versatility of spray pyrolysis technique is demonstrated relating to metal oxides, metallic spinel oxides, binary, ternary, quarternary chalcogenides, and superconducting films [35]. Despite its simplicity, spray pyrolysis has the following advantages.

1. It offers an extremely easy way to dope films with virtually any element in any proportion by merely adding it to the spray solution.

2. Spray pyrolysis does not require any high quality targets and/or substrates nor require vacuum at any stage.

3. The deposition rate and the thickness of the film can be easily controlled over a wide range by changing the spray parameters.

4. Operating spray pyrolysis deposition at moderate temperatures, films on less robust materials can be produced.

5. Unlike high power methods, it does not cause local overheating thereby impose no restriction on selecting substrate material.

6. By changing composition of the spray solution, it can be used to make layered films and films having composition gradient throughout the thickness.

7. Prepared films are compact and uniform and the necessary reliable kinetic data can be obtained from the film surface.

8. Large area coating and high reproducibility are quite possible.

9. It can be in-built in the laboratory with greater ease and the film production cost is very low when comparing with the other deposition techniques.
1.7.3. Some other thin film deposition techniques

1.7.3.1. Dip coating technique

Dip coating technique can be described as a process where the substrate to be coated is immersed in a liquid and then withdrawn with a well-defined withdrawal speed under controlled temperature and atmospheric conditions. The coating thickness is mainly defined by the withdrawal speed, by the solid content and the viscosity of the liquid. If the withdrawal speed is chosen such that the sheer rates keep the system in the Newtonian regime, the coating thickness can be calculated by the Landau-Levich equation [36] (eq 1).

\[ h = 0.94 \left( \frac{\eta}{\gamma A} \right)^{1/2} \left( \frac{g}{\rho \gamma A} \right)^{1/4} \frac{r_0^4}{w} \]  

(1)

Where \( h \) = coating thickness, \( \eta \) = viscosity, \( \gamma_A \) = liquid-vapour surface tension, \( \rho \) = density, \( g \) = gravity. For an acid catalyzed silicate sol, thicknesses obtained experimentally fit very well to calculate ones [37]. The interesting part of dip coating processes is that by choosing an appropriate viscosity the coating thickness can be varied with high precision from 20 nm up to 50 \( \mu \)m while maintaining high optical quality. The schematics of a dip coating process are shown in Fig 1.11. If reactive systems are chosen for coatings, as it is the case in sol-gel type of coatings using alkoxides or pre-hydrolyzed systems - the so-called sols - the control of the atmosphere is indispensable. The atmosphere controls the evaporation of the solvent and the
Fig. 1.11 Stages of the dip coating process
subsequent destabilization of the sols by solvent evaporation, leading to a gelation process and the formation of a transparent film due to the small particle size in the sols (nm range) [38]. This is schematically shown in Fig. 1.12. In general, sol particles are stabilized by surface charges, and the stabilization condition follows the Stern’s potential consideration. According to Stern’s theory the gelation process can be explained by the approaching of the charged particle to distances below the repulsion potential. Then the repulsion is changed to an attraction leading to a very fast gelation. This takes place at the gelation point (Fig. 1.12). The resulting gel then has to be densified by thermal treatment, and the densification temperature depending on the composition. But due to the fact that gel particles are extremely small, the system shows a large excess energy and in most cases a remarkably reduced densification temperature compared to bulk-systems is observed. However, it has to be taken into consideration that alkaline diffusion in conventional glasses like soda lime glasses starts at several hundred degrees centigrade and alkaline ions diffuse into the coated layer during densification. In most cases, this is of no disadvantage, as the adhesion of these layers becomes perfect, but influences on the refractive index have to be taken into consideration for the calculations for optical systems. Dip coating processes are used for plate glass [39-41]. Recently, an angle-dependent dip coating process has been developed [39,42]. Control of layer thickness is important for optical coatings, and can be realized by Landau-Levich’s equation with high precision. The coating thickness is dependant on the angle between the substrate and the liquid surface
Fig. 1.12 Gelation process during dip coating process, obtained by evaporation of the solvent and subsequent destabilization of the sol
Layer thickness can be calculated including the dipping angle and different layer thickness can be obtained on the top and bottom side of the substrate (Fig. 1.13). The calculations showed that the number of layers can be reduced drastically to obtain similar optical properties to get with layers of one and the same thickness. Dip coating processes have been developed for curved surfaces like eye-glass lenses, mainly to employ scratch resistant coatings for plastic substrates.

Variations of dip coating processes are employed for fiber coatings in optical fiber industry, where the fibers are drawn through a coating liquid (mainly polymers) to protect the surface from mechanical impacts. The drawbacks of large scale dip coating are the difficult handling of large panes and the stability of the dipcoating baths under atmospheric conditions. The development of easy to handle materials and techniques is necessary.

1.7.3.2. Spin coating process

In the spin coating process, the substrate spins around an axis which should be perpendicular to the coating area. The spin-on process has been developed for the so-called spin-on glasses in microelectronics and substrates with a rotational symmetry, e.g. optical lenses or eye glass lenses. The schematics are shown in Fig. 1.14. Fully automated spin coating processes have been introduced in the ophthalmic glass industry under clean room conditions and fully automated handling. The coating thickness varies between several hundreds of nanometers and up to 10 micrometers.
Fig. 1.13 Schematic diagram of angle dependent dip coating
Substrate

N'acuuni chuck

Deposited Precursor

Fig. 1.14 Schematic diagram of spin coating unit
Even with non-planer substrates very homogeneous coating thickness can be obtained. The quality of the coating depends on the rheological parameters of the coating liquid, and it has to be mentioned, that one should operate in the Newtonian regime. Another important parameter is the Reynolds number of the surrounding atmosphere. If the rotation velocity is in a range that the atmospheric friction leads to high, Reynolds numbers (turbulences) disturbances in the optical quality are observed. The dependence of the final thickness of a spin coated layer on the processing and materials parameters like angular velocity, viscosity and solvent evaporation rate by the semi-empirical formula given in equation 2 [43].

\[
h = \left(1 - \rho_\lambda / \rho_{\lambda_0}\right) \left(\frac{3\eta \cdot m}{2\rho_{\lambda_0} \cdot \omega^2}\right)^{1/2} \quad (2)
\]

\( \rho_\lambda \) = mass of volatile solvent per unit volume

\( \rho_{\lambda_0} \) = initial value of \( \rho_\lambda \)

\( h \) = final thickness

\( \omega \) = angular speed, \( \eta \) = viscosity

\( m \) = evaporation rate of the solvent

Since \( m \) has to be determined empirically any way, the more simple formula, given in equation 3 may be used:

\[
h = A \cdot \omega^B \quad (3)
\]
Where $A$ and $B$ are constants to be determined empirically. Thickness of films obtained by spin coating, using different angular speeds, and their results could be fitted very well with equation 3 [44-46]. $B$ was determined to be in the interval between 0.4 and 0.7, which is in rather good agreement with equation 2, where the exponent for $w$ is 0.67.

1.7.3.3. Ultrasonic spray pyrolysis technique

Fig.1.15 shows a schematic diagram of the experimental apparatus. The spray-pyrolysis system mainly consists of an ultrasonic nebulized [47], a reaction furnace and an electrostatic precipitator. The laminar flow aerosol reactor used in the present study was a high-quality ceramic tube of 20 mm inner diameter and about 1500 mm long. The electronic furnace consists of six heating zones, each 180 mm in length, separated by about 5 mm insulation zones. The temperature of each heating zone was controlled to within 2K with a temperature controller: $T_1$, $T_2$, $T_3$, $T_4$, $T_5$ and $T_6$ indicate the wall temperatures at the middle of the each heating zone. Fig.1.16 shows the axial temperature profiles in the reactor for two typical cases: i) constant and ii) increasing temperature distributions.

The starting solution was atomized at a frequency of 1.75 MHz by the ultrasonic nebulizer. The generated droplets were carried to the reaction furnace by air, with a flow rate ranging from 0.5 to 4 dm$^3$/min. If we assume the plug flow in the reactor, the residence time ranges from 5 to 42 s for the flow rates. The particles generated from the furnace were collected using an electrostatic precipitator, which was maintained at around 473 K, to avoid the condensation of water on the particles. The feed solution was
Fig. 1.15 Schematic diagram of ultrasonic spray pyrolysis experimental setup
Fig. 1.16 Observed axial temperature profiles in the reactor
prepared by dissolving the required amounts of salts were dissolved in to distilled water. The concentrations of the precursor solutions were 0.05 - 0.1 mol/dm³, respectively.

1.7.3.4 Electrostatic spray pyrolysis technique

It is a spray deposition technique [48] in which (unlike other spray techniques) the spray of a precursor solution is generated by an electrohydrodynamic (EHD) force. The schematic of the setup used in this study is shown in Fig. 1.7. A DC voltage (in the range 0-20 kV) is applied between an electrically conductive substrate such as a metal or ITO glass and a metal capillary nozzle, which is connected to a precursor solution. Under a hydrodynamic pressure and/or an applied gas pressure, a certain flow rate of the precursor solution can be achieved at the nozzle. When the DC voltage is increased to a certain onset value (usually above 5 kV) the solution is atomized at the orifice of the nozzle, hence, a spray is generated. The onset DC voltage mainly depends on the nozzle-substrate distance and the physical properties of the precursor solution, especially its electrical conductivity, due to pyrolysis of the precursors, a thin layer is deposited on the substrate surface.

It is common practice to use alcohols as solvent for adequate solubility of many inorganic salts to be used as precursors. The deposition kinetics and thus the layer morphology are influenced by many factors, including substrate temperature, flow rate and physical properties of the precursor solution, as well as the evaporation of the solvent before the spray of droplets reach the substrate temperature.
Fig. 1.17 Schematic diagram of electrostatic spray deposition setup
REFERENCES
