

# **CHAPTER 2**

## **Literature Review**

## **2.1 Electrochemical Power Sources or Batteries**

A battery is an electrochemical device, which converts chemical energy into electrical energy by redox reactions, which occurs at the electrodes. The term battery refers to one or more cells connected in series or parallel or both.

The electrochemical cell consists of three main components:

1. The anode or negative electrode - the reducing electrode - undergoes oxidation during the electrochemical reaction.
2. The cathode or positive electrode - the oxidizing electrode- undergoes reduction during the electrochemical reaction.
3. The electrolyte - the ionic conductor - which provides the medium for the transfer of ions between the anode and cathode. The electrolyte is usually a liquid, such as water or other solvents, with dissolved salts, acids or alkalis to improve ionic conductivity. Some batteries use solid electrolyte, which function as both a separator and electrolyte (Koksbang et al, 1994).

The ideal battery should consist of anode and cathode made up of the lightest material and a high cell voltage and capacity. It is not always possible to have the above combinations due to reactivity with other cell components, polarization, difficulty in handling, high costs and other deficiencies (Linden, 1994).

The criteria used for selecting an anode, cathode and the electrolyte are given in Table 2.1 (Jacob, 1999; Koksbang et al, 1999).

Table 2.1: Criteria for selection of anode, cathode and electrolyte (Jacob, 1999; Koksbang et al, 1999)

Anode	Cathode	Electrolyte
Efficient reducing agent	Efficient oxidizing agent	Good ionic conductivity
High coulombic output (Ah/g)	Use working voltage	Zero electronic conductivity
Good conductivity	Good conductivity	Electrochemically stable
Stable (when contact with electrolyte)	Stable (when contact with electrolyte)	Chemically and electrochemically compatible with electrode materials.
Ease of fabrication	Ease of fabrication	Safeness in handling
Low cost	Low cost	Low cost
		Good thermal stability.

## 2.2 Operation of a Cell

### 2.2.1 Discharge

The operation of a cell during discharge is shown schematically in figure 2.1.

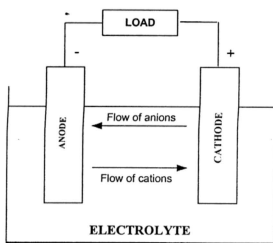


Figure 2.1: Electrochemical operation of a cell discharge.

Example:

Negative Electrode : Anodic Reaction (oxidation)  
 $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}$

Positive Electrode : Cathodic Reaction (reduction)  
 $\text{Cu}^{2+} + 2\text{e} \rightarrow \text{Cu}$

Overall Reaction :  $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$   
(discharge)



### 2.2.2 Charge

During recharge, oxidation takes place at the positive electrode and reduction at the negative electrode, as shown in figure 2.2.

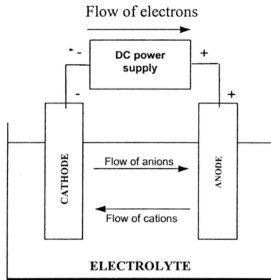


Figure 2.2: Electrochemical operation of a cell (charge)

Example :

Negative Electrode : Cathodic Reaction (Reduction)  
 $\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$

Positive Electrode : Anodic Reaction (oxidation)  
 $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$

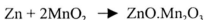
Overall Reaction (charge) :  $\text{Mg}^{2+} + 2\text{Cl}^- \rightarrow \text{MgCl}_2$

## 2.3 Batteries

### 2.3.1 Primary Cells or Batteries

1. Leclanché
2. Magnesium
3. Alkaline  $\text{MnO}_2$
4. Mercury
5. Mercad
6. Silver oxide
7. Zinc/air
8.  $\text{Li/SO}_2$
9.  $\text{Li/MnO}_2$

A primary system is one, that has its useful life is ended once its reactants have been consumed during the discharge process. Primary cells or batteries have existed more than 100 years. The most popular and widely used of all the primary batteries is zinc-carbon (Leclanché). The zinc-carbon cell uses a zinc anode, a manganese dioxide or graphite cathode and an electrolyte of ammonium chloride or zinc chloride dissolved in water. As the cell is discharged, the zinc is oxidised and the manganese dioxide is reduced. A simplified reaction is



Main advantages of primary batteries are, that they are convenient, simple, and easy to use, can be sized and shaped to fit their application, good shelf life, reasonable energy and power density, reliability and acceptable cost.

### **2.3.2. Secondary or Rechargeable Cells or Batteries**

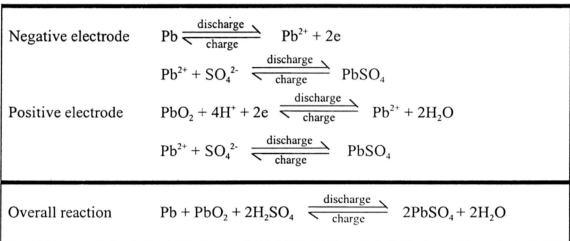
1. Lead - Acid
2. Edison
3. Nickel - Cadmium
4. Silver - Zinc
5. Nickel - Zinc
6. Nickel - Hydrogen
7. Nickel - Metal Hydride
8. Silver - Cadmium
9. Zinc/Chlorine
10. Zinc/Bromine
11. Lithium/Manganese dioxide
12. Lithium/Iron disulphide

A secondary system is one, which can be charged by passing a current through the opposite cell in the opposite direction to that of discharge.

Secondary batteries fall into two main categories (Linden , 1994):

1. It can be used as an energy storage device, being charge by a primary energy source and delivering its energy to the load on demand. Examples are automotive and aircraft systems, emergency no-fail and standby power sources, and stationary energy storage (SES) system for electric utility load leveling.
2. It can be used or discharged essentially as a primary battery but recharged after use rather than being discarded. For example, in consumer electronic, electric vehicle, for cost savings (as they can be recharged rather than replaced) and its applications requiring power drains beyond the capability of primary batteries.

The most widely used secondary batteries is the lead-acid battery developed by Planté in 1859. The battery uses lead dioxide as the active material of the positive electrode and metallic lead as the negative active electrode. The electrolyte is a sulphuric acid solution. As the cell discharges, both electrodes are converted to lead sulphate. The processes reverses on charge:



In recent years, rechargeable batteries have found important new applications in expanding markets, such as portable computers (laptops) and telecommunication equipments. The interest in electric vehicles has stimulated research on rechargeable batteries. Much of the attention has been focussed on lithium batteries. Small rechargeable lithium batteries, available on the market today, show specific energies of 100 - 200 Wh kg<sup>-1</sup>. The upper limit surpasses those of aqueous electrolyte counterparts (nickel - cadmium or nickel - metal hydride) by a factor of 1.5 - 2 (Beck and Rüetschi, 2000).

#### **2.4 Why Lithium Batteries ?**

The success of a battery system depends on three important criteria (Beck and Rüetschi, 2000):

1. Energy (high energy content with respect to unit weight and volume)
2. Economics (low manufacturing costs, low maintenance during use, long service life)
3. Environment (free of toxic materials, safe, low energy consumption during manufacture and use, long service life, high reliability, easy to recycle).

Most of the commercially available batteries may not satisfy the above three important criteria. For example, Ni-Cd, Ni-metal hydride, lead acid and zinc-carbon have low specific capacity. These batteries have a limited open circuit potential

1.23V (theoretically), high self-discharge rate and short shelf life. The use of batteries containing cadmium and lead have an impact on environment, as they are toxic.

Lithium battery system is preferred. This is because among all the elements in the periodic table, lithium is the one that combines the highest specific capacity of nearly 4Ah/g with an extremely negative potential (-3.0 V versus SHE). These features promise cells of high voltage and high specific capacity thus high energy density. (Prabaharan and Radhakrishna,1997; Jones and Akridge, 1994). Li cells also have long cycle-life, for example, Li/TiS<sub>2</sub> cell have obtained 200 - 300 cycles at full depth-of-discharge and up to 1000 cycles at 50 per cent depth-of-discharge. The Ragone plots given in figure 2.3 for Ni-Cd and Li/TiS<sub>2</sub> cells illustrate the superior capabilities of Li systems (Abraham, 1993).

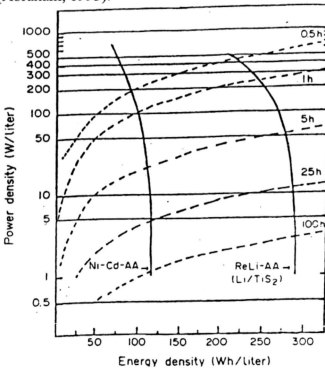


Figure 2.3: Comparison of secondary Li/TiS<sub>2</sub> and Ni/Cd cells. The Li cell is the ReLi cell manufactured by EIC.

## 2.5 Lithium Batteries

### 2.5.1 Lithium Primary Batteries

Research into lithium batteries began in the 1950s when it was noticed that Li-metal was stable in a number of non-aqueous electrolytes such as fused salts, liquid  $\text{SO}_2$  or organic electrolytes such as  $\text{LiClO}_4$  in propylene carbonate (Brandt, 1994). This stability was due to the formation of passivation layer on the metal that prevents lithium from chemically reacting with the electrolyte but allows lithium to go into solution during cell discharge. Lithium primary batteries were commercialised in the late 1960s.

Lithium primary batteries using lithium as anode have many advantages over conventional batteries. They have high voltage, high energy density, operates over a wide temperature range, good power density, flat discharge characteristic and superior shelf life.

Lithium primary batteries are used in a variety of applications. For example, lithium/iodine-polyvinylpyridine cells are used as power source for pacemakers and lithium/sulphur dioxide cells were used in NASA Galileo probe to investigate the atmosphere of Jupiter (Vincent, 2000).

### 2.5.2 Lithium Secondary Batteries

Over the past 20 years, the rechargeable lithium cells such as Li/TiS<sub>2</sub>, Li/MoS, Li/NbSe<sub>3</sub>, Li/MnO<sub>2</sub> have been developed and demonstrated in prototype cells. These cells operating at room temperature offer several advantages compared to conventional aqueous technologies, including higher energy density, higher cell voltage and longer charge retention (Hossain, 1994).

Large-volume practical secondary batteries using lithium metal as a negative electrode has not been successful due to safety problems. The difficulties associated with the use of metallic lithium stems from its reactivity to essentially all electrolyte (Anderman, 1994). During charging, Li metal is replated on the anode and some of this lithium metal reacts with the electrolyte, become passivated and permanently isolated from the bulk anode as finely divided lithium (Abraham, 1993). Finely dispersed lithium does not cause the electrolyte to be unstable, as long as lithium is passivated by the electrolyte. However, if the cell is abused, that is, the temperature is raised above the melting point of lithium, passivity is lost and the cell can vent with flame. Temperature of the cell can be raised by electrical abuse e.g. internal or external shorts. Internal shorts occur because the plated lithium is not uniform and after many charge/discharge cycles, the dendrites will make contact with the cathode.



### 2.5.3 Lithium Ion Batteries or Rocking-chair Batteries

In the early 1980s' it was suggested the lithium metal anode in the lithium secondary batteries were replaced with a lithium intercalation compound which had a much lower chemical potential versus than the lithium intercalation compound chosen for the cathode. This was to overcome the shortcomings of using a lithium anode. During charge and discharge lithium ion rocks back and forth between the electrodes. This lithium battery, free of lithium metal was originally termed "rocking chair" (RCB) by Armand.

$\text{LiWO}_2$ ,  $\text{LiMnO}_2$  and  $\text{LiC}_6$  were suggested as negative electrode materials. The energy density of a system using the two oxides were not attractive. Lithium graphite has a chemical potential close to that of metallic lithium and a specific capacity of  $372 \text{ Ah g}^{-1}$ . However, severe problems of exfoliation were experienced in organic electrolytes, limiting the apparent viability to polymer electrolyte cells (Broussely et al, 1999). The rocking chair concept was not pursued further until late 1980s.

In 1990 Sony Energy Tech Inc., managed to produce successfully the first commercial lithium ion battery using a non-graphitic carbon anode and a  $\text{LiCoO}_2$  cathode. This was followed by several Japanese companies successfully producing their own version of lithium ion rechargeable batteries. The table below gives the names of some Japanese companies producing lithium ion batteries. These companies are also active in research and development of lithium ion batteries.

Table 2.1: Monthly production of lithium ion portable batteries  
(Katz et al, 1998).

	Million units manufactured per month	Date of forecasts
Asahi - Toshiba	1.6	mid - 1996
Fujifilm	1.5	1998
Hitachi - Maxell	6	July 1997
Japan Storage	3	April 1997
Matsushita	20	1999
Matsushita US	1.5	1997
Moli Energy Canada	10	2000
Nippon Moli	2	January 1998
Sanyo	5	September 1996
Sony	10	March 1997
	20	1999

## 2.6 Intercalation

Intercalation reaction can be defined as a reversible insertion of mobile guest species into a rigid host lattice without significant structural modification of the host. (Krovin, 1997; Ouvard and Guyomard, 1996; Narukawa et al, 1999; Imanishi et al, 1999; Young-Min Choi and Su-Il Pyun, 1997), such reaction is favoured by host materials which has low dimensionality and was initially observed in graphite and lamellar transition metal chalcogenides. These compounds have layered structures and depending on their packing they may have empty octahedra, trigonal prisms or tetrahedra. These sites are available for guest species and favours their diffusion. The intercalation reaction between the solid host and guest species occurs spontaneously at ambient temperatures. In general the reaction temperature should

be high enough to ensure mobility of the guest species but not so high so that the structure of the lattice is modified due to breaking of strong bonds.

Intercalation chemistry is important in lithium ion batteries. It involves lithium ion transferred between the anode and cathode as the cell is cycled. This is shown in figure 2.4. The positive electrodes are usually lithium transition metal oxide, which act as a source of 'lithium ions' and the negative electrodes are usually graphitized carbon. The cells are fabricated in discharged state. On charging lithium ions and electrons intercalate with the negative electrode. During discharge, the lithium ions will be deintercalated from the graphitized carbon electrode.

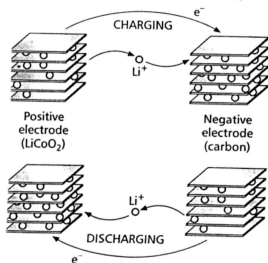
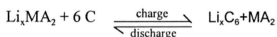


Figure 2.4: Charging and discharging lithium ion battery ( Lister and Renshaw,2000).

### 2.6.1 Model Scheme of Lithium Intercalation into Graphitized Carbon (Satoh et al, 1995).

Lithium intercalated graphite and carbon materials have been proposed for applications as negative electrode in lithium batteries. Carbon materials can be distinguished into two main types, graphitized carbon and disordered carbon, on the basis of crystal structure. Graphitized carbon consists of graphite structures and some turbostratic layers which are stacked with random translations and rotations between adjacent carbon hexagonal layers. Disordered carbons are made up of small crystallites which have buckled turbostratic disordered structures and unorganised carbons connecting each crystallite.

In order to explain the actual intercalation process in these graphitised carbon materials, various experiments have been performed using electrochemical measurements and X-ray diffractions. It can be concluded that, lithium competitively intercalates into the graphite crystallites and turbostatic disordered layers, which exist in the host graphitized carbon. The model scheme is represented in figure 2.5.

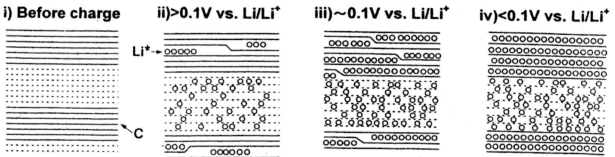


Figure 2.5: The schematic drawings of lithium intercalation into graphitized carbon with charge voltage range graphitized carbon with charge voltage range. Graphite layers are displayed with solid lines and turbostratic disordered layers with dash lines (Satoh et al, 1995).

Explanation :

- (i) The host graphitized carbon consists of the stacking structure of graphite crystallites (solid line) and turbostratic disordered layers (dash line).
- (ii) The lithium is mainly intercalated in turbostratic disordered layers above 0.1V versus Li/Li<sup>+</sup> ( $x < 0.2$  in Li<sub>x</sub>C<sub>6</sub>).
- (iii) The average layer spacing increased slightly with the lithium intercalation in the region of  $x = 0.2 - 0.5$  because of the influence of lithium intercalation into turbostratic disordered layers. In this region, the charge voltage is near 0.1V versus Li/Li<sup>+</sup> and lithium can be intercalated into graphite crystallites as much as turbostratic disordered layers.
- (iv) In the region below 0.1V versus Li/Li<sup>+</sup> ( $x > 0.5$ ), lithium is intercalated into graphite crystallites rather than turbostratic layers. This is because turbostratic structure has less available site for lithium intercalation than graphite structure in this voltage region.

### 2.6.2 Requirements of Insertion Electrode Materials (Scrosati, 1993; Korovin, 1997)

The successful operation of a lithium ion battery will depend on conditions fulfilled by the selected insertion electrode materials. They are as follows :

- (i) the lithium activity in the negative electrode must be close to 1 in order to assure open circuit voltage approaching those obtainable with pure lithium;
- (ii) low molecular weight and volume;
- (iii) high diffusion coefficient of lithium ion in both positive and negative electrodes;
- (iv) minimum voltage changes upon lithium ion intake and release between in both electrodes to limit and release between in both electrodes to limit fluctuations during charged and discharge cycles;
- (v) insoluble, low corrosion rate and compatible with electrolyte;
- (vi) easy to fabricate an based on non-toxic compounds, to assure low cost and environmental control.

### 2.6.3 Why 3d-transition metal dioxides are preferred as intercalation materials?

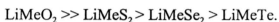
For practical batteries, space rather than weight is the limiting factor in designing batteries. In other words, volumetric capacity is more important parameter than gravimetric capacity in considering battery materials. Based on hard sphere model, the volumetric capacities of insertion materials are optimised when electrochemical reaction proceeds in topatactic manner;



- (oct) - octahedral
- (cp) - closest packed
- $\square$  - vacant octahedral sites
- Me - transition metal
- X -  $\text{O}^{2-}$ ,  $\text{S}^{2-}$ ,  $\text{Se}^{2-}$  or  $\text{Te}^{2-}$

Ohzuku (1994) and Ohzuku (1998) calculated volumetric capacities of divalent anions, such as  $O^{2-}$ ,  $S^{2-}$ ,  $Se^{2-}$  and  $Te^{2-}$ . The volumetric capacities of  $LiMeX_2$  were  $1.43 \text{ Ah cm}^{-3}$  for  $LiMeO_2$ ,  $0.63 \text{ Ah cm}^{-3}$  for  $LiMeS_2$ ,  $0.51 \text{ Ah cm}^{-3}$  for  $LiMeSe_2$  and  $0.36 \text{ Ah cm}^{-3}$  for  $LiMeTe_2$  assuming a closest – packed anion array in which the transition metal ions and lithium ions are located at the octahedral sites in their suitable sizes.

The volumetric capacity is in the order



It can be concluded that  $LiMeO_2$  is the candidate material for battery application.

This is better illustrated in figure 2.6.

Operating voltage is another important parameter when considering battery materials. From figure 2.7, shows the approximate operating voltages of transition metal (di)oxides in nonaqueous lithium cell. The upper and lower lines indicate 3d- and 4d-transition metal (di)oxides respectively. The relationship between operating voltages and d-electron character can be clearly seen. The operating voltage is in the order:

3d-transition metal (di)oxide > 4d transition metal (di)oxide > 5d-transition metal (di)oxide

The above two reasons justify the choice of selecting 3d-transition metal dioxides as positive electrode material in lithium ion batteries.



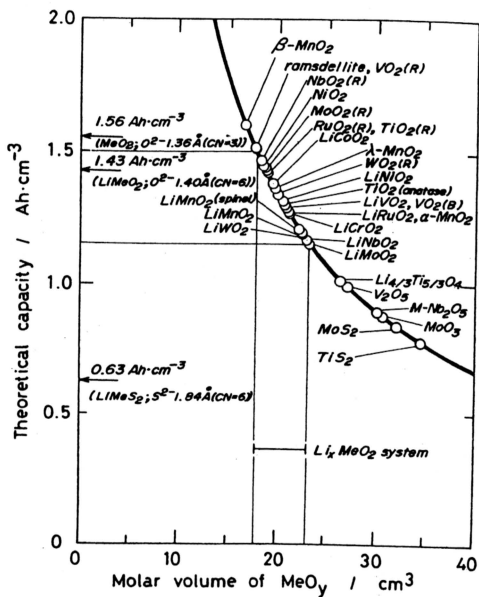


Figure 2.6: The volumetric capacity in Ah cm<sup>-3</sup> versus the molar volume of MeO<sub>y</sub> in cm<sup>3</sup> for transition metal (di)oxides. MoS<sub>2</sub> and TiS<sub>2</sub> are also shown in comparison (Ohzuku, 1998).

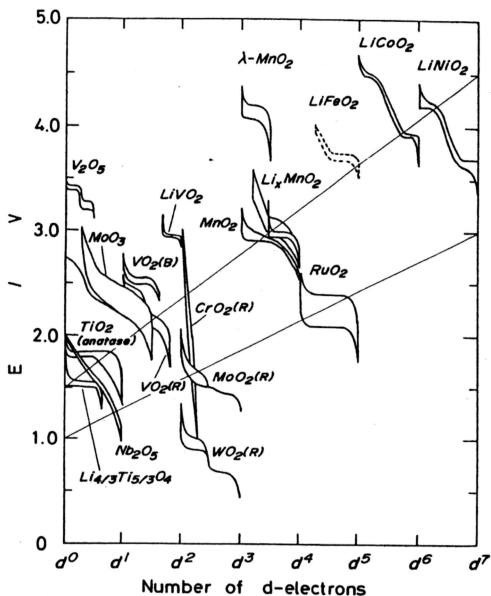


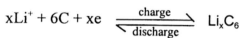
Figure 2.7: Approximate operating voltages of transition metal (di)oxides in non aqueous lithium cells. Relation between the operating voltages and the number of d - electron can be seen (Ohzuku, 1998).

## 2.7. Electrode Materials

### 2.7.1 Anode Materials

Conventional anodes used in rechargeable lithium-ion batteries use various kinds of carbon-based materials (Zhong et al, 2000) carbon graphite has been the most favoured anode material (Beck and Rüetschi, 2000). This can be partly attributed to its low cost material per battery industry. Initial attempts to use graphite as negative host structure failed due to electrode disintegration. The situation changed with the finding that poorly crystalline carbons are less sensitive to decomposition. Its capacity was modest when compared to graphite. Crystalline carbon materials regained interest when  $\text{LiC}_6$  stoichiometry was actually achieved with a careful design of electrolyte composition mainly based on ethylene carbonate (Broussely et al, 1999).

Graphite has a layered structure and it can reversibly insert lithium ion according to the following reaction:



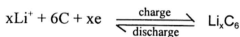
The potential of graphite will be similar to that of pure lithium by increasing  $x$  (Rahner et al, 1996). This is another advantage using carbon graphite anode.

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Lithium metal alloys are attractive as anode material on the basis of volumetric and gravimetric capacity. The problem with metal alloys is that there is two and sometimes threefold volume change associated with alloying of lithium. This can cause the “cracking” and “crumbling” of the alloy anode, and subsequently the conductivity of the electrode is reduced and the internal resistance of the cell is increased, resulting in poor cycleability (Courtney and Dahn, 1997). In the case of carbon, the volume difference during the formation of  $\text{LiC}_6$  is much less. It is about 9.4%. Therefore carbon graphite is the favoured anode material and it has a maximum theoretical capacity of  $372 \text{ mAhg}^{-1}$  (Li et al, 1999; Broussely et al, 1999; Scrosati, 2000).

A new class of materials such as perovskite - type oxide of the type  $\text{ABO}_3$  (Zhong et al, 2000), amorphous tin-based composite oxide (Wang et al, 1998), metal vanadates (Ouvard and Guyomard, 1996) and lithiated metal nitrides (Broussely et al, 1999) have been investigated as a possibility as an anode material for future lithium ion batteries.

### **2.7.2 Cathode Materials**

Lithium transition metal oxides,  $\text{LiM}_x\text{O}_2$  ( $M = \text{Ni, Co, Mn}$ ) are often suggested as cathode materials for lithium ion batteries (Amatucci et al, 1996; Jacob et al, 2000; Nakamura et al, 1999; Lee et al, 2000; Liu et al, 2000; Yan et al, 1998). The layered  $\text{LiCoO}_2$  and  $\text{LiNiO}_2$  have theoretical capacity double that of  $\text{LiMn}_2\text{O}_4$  due to one-to-

one ratio of lithium to transition metal (Amatucci et al,1996). Since more than 0.5 lithium cannot be reversibly deintercalated from the structure due to structural instabilities, the three cathode materials have similar capacities. Copper oxides (Arai et al, 1998; Jacob et al, 2000) and vanadium oxides (Kawita et al, 1998, Kawita et al, 1999) have also been investigated as possible cathode materials for lithium ion batteries.

### 2.7.2 ( a ) Lithium Manganese Oxides

Considerable research has been devoted to manganese oxide insertion compound and in particular, the three-dimensional  $\text{LiMn}_2\text{O}_4$ , Reasons for interest in this material are (Broussely et al, 1999; Liu et al, 2001) :

- (i) familiarity of the battery manufacturing industry on manganese compounds
- (ii) a larger thermal stability domain especially when overcharged
- (iii) a higher discharge voltage useful for telecommunication appliances
- (iv) a potential lower cost of manganese than nickel or cobalt
- (v) more friendly impact on environment

However,  $\text{LiMn}_2\text{O}_4$  has some shortcomings (Broussely et al, 1999)

- (i) low specific capacity (i.e. limited to around  $120 \text{ mAhg}^{-1}$ )
- (ii) lower power than layered ( $\text{LiNiO}_2$ ,  $\text{LiCoO}_2$ )
- (iii) fading and storage losses are very high, especially with increasing temperatures.

There is no general consensus as to the reasons for capacity fading but the following causes have been indicated (Wu et al, 2000)

- (i) spinel dissolution
- (ii) structural instability in charged state
- (iii) electrolyte decomposition, and
- (iv) Jahn-Teller effect

To improve the performance of  $\text{LiMn}_2\text{O}_4$  it has been suggested

- (i) partially substitute the manganese with transition metals. Substitution of manganese by cobalt, chromium or nickel brought about decrease in capacity ( $100\text{-}110 \text{ Ah kg}^{-1}$ ) but improved cycling performance. (Song and Ahn, 1998; Hosaya et al, 1998; Hernan et al, 1999)
- (ii) low temperature synthesis (Guan and Liu, 1998; Huang and Bruce, 1994; Prabakaran et al, 1998)

### 2.7.2 (b) Layered Lithium Metal Oxides

Stoichiometric  $\text{LiCoO}_2$  and  $\text{LiNiO}_2$  are isostructural and possess a crystal structure consisting of alternative layers of trigonally distorted  $\text{MO}_6$  and  $\text{LiO}_6$  octahedra sharing edges ( $\alpha$  -  $\text{NaFeO}_2$  types structure) (Zhecheva and Stayanova, 1993; Jang et al, 1999; Nakamura et al, 1999; Gummow and Thackeray, 1992). Figure 2.8 shows structure of  $\text{LiNiO}_2$ . The theoretical capacity for  $\text{LiCoO}_2$  and  $\text{LiNiO}_2$  is about  $275 \text{ mAh g}^{-1}$ . However, the actual theoretical capacity for both cells are lower. Refer to tables 2.2 and 2.3.

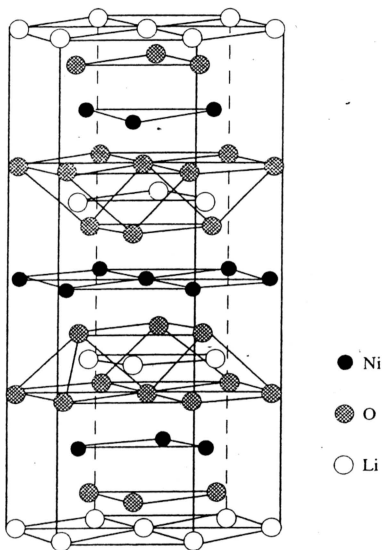


Figure 2.8: Crystal structure of  $\text{LiNiO}_2$  (Korovin, 1998)



Table 2.2

Theoretical specific capacities and energies for various cathode reactions (Ritchie et al, 1999)

	Capacity (mAhg <sup>-1</sup> cathode)	Average Voltage	Specific density (W h kg <sup>-1</sup> chatode)
LiCoO <sub>2</sub> → Li + CoO <sub>2</sub>	274	3.6	986
LiNiO <sub>2</sub> → Li + NiO <sub>2</sub>	275	3.6	990
LiMn <sub>2</sub> O <sub>4</sub> → Li Mn <sub>2</sub> O <sub>4</sub>	148	3.8	562
LiNi <sub>0.8</sub> Co <sub>0.2</sub> → Li + Ni <sub>0.8</sub> Co <sub>0.2</sub> O <sub>2</sub>	274	3.6	986
LiMnO <sub>2</sub> → Li + MnO <sub>2</sub>	286	3.2	914
2VO <sub>2</sub> .Li <sub>2</sub> SO <sub>3</sub> → Li + 2VO <sub>2</sub> LiSO <sub>3</sub>	206	3.5	722

Table 2.3

A comparison of experimental specific energies for different cathode materials (Ritchie et al, 1999)

Cathode	Apparent charging reaction	Reported capacity (mAhg <sup>-1</sup> )	% of theoretical capacity
LiCoO <sub>2</sub>	LiCoO <sub>2</sub> → 0.58Li + Li <sub>0.42</sub> CoO <sub>2</sub>	142	52
LiNiO <sub>2</sub>	LiNiO <sub>2</sub> → 0.53Li + Li <sub>0.47</sub> NiO <sub>2</sub>	145	53
LiNi <sub>0.8</sub> Co <sub>0.2</sub>	LiNi <sub>0.8</sub> Co <sub>0.2</sub> O <sub>2</sub> → 0.66Li + LiNi <sub>0.14</sub> Co <sub>0.2</sub> O <sub>2</sub>	180	66
LiMn <sub>2</sub> O <sub>4</sub>	LiMn <sub>2</sub> O <sub>4</sub> → 0.74Li + Li <sub>0.26</sub> Mn <sub>2</sub> O <sub>4</sub>	120	81

At present LiCoO<sub>2</sub> is widely used in commercial lithium ion batteries. The actual specific capacity of LiCoO<sub>2</sub> is 142 mAh g<sup>-1</sup> without appreciable loss of specific capacity over many charge-discharge cycles. Advantages of LiCoO<sub>2</sub> is that, it is easy to prepare and gives higher voltages, and better reversibility in Li/LiMO<sub>2</sub> cells (Kang et al, 1999).

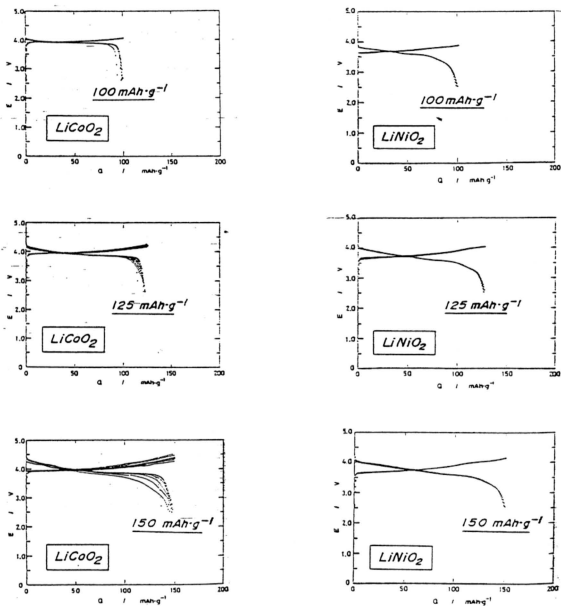


Figure 2.9: Charge and discharge curve of Li/LiCoO<sub>2</sub> and Li/LiNiO<sub>2</sub> cells operated at a rate of 0.17 mA cm<sup>-2</sup> at 30°C. Electrolytes used was 1M LiClO<sub>4</sub>- propylene carbonate (PC) solution (Ohzuku,1998).

LiNiO<sub>2</sub> is in the improvement stage for practical applications. LiNiO<sub>2</sub> shows higher rechargeable capacity than LiCoO<sub>2</sub> as shown in figure 2.9. From a practical viewpoint, it is more favourable to use LiNiO<sub>2</sub> electrode in lithium-ion batteries since

nickel is cheaper than cobalt (Choi et al, 1996; Lee et al, 1999; Zhecheva and Stayanova, 1993). Moreover,  $\text{LiNiO}_2$  which shows a lower potential than  $\text{LiCoO}_2$  during charge, is less oxidizing versus the electrolyte (Caurant et al, 1996). However, the  $\text{LiNiO}_2$  are more difficult to synthesise than  $\text{LiCoO}_2$ , because of the tendency to form nickel rich non-stoichiometry phase (Rougier et al, 1996).  $\text{LiCoO}_2$  can be prepared by sintering a mixture of almost any Li, Co and O sources under proper temperature conditions, whereas the  $\text{LiNiO}_2$  compound need to be prepared under strong oxidizing conditions (Koksbang et al, 1996).

$\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$  is attractive choice of cathode material in Li-ion cells due to its cost advantage and increased capacity compared with  $\text{LiCoO}_2$  (Weaving et al, 2000). In comparison to  $\text{LiNiO}_2$ ,  $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$  exhibits better thermal stability (Kim and Sun, 1998) and increased reversibility due to cobalt ions stabilising the crystallographic structure (Molenda et al, 1999; Levi et al, 1999). In fact these compounds are able to offer a stable cycleability on the  $180 \text{ mAh g}^{-1}$  and improves the environmental compability when nickel content to cobalt ( $\text{Li Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ ) is high (Scrosati, 2000).

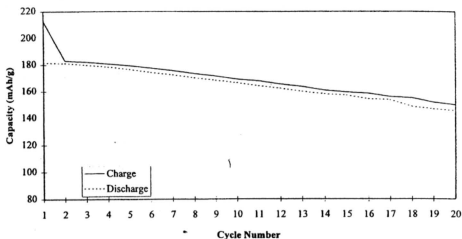


Figure 2.10: Cycling performance of a  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  cell at the C/A rate over the voltage range 2.5 to 4.5 V. Cycle number against specific capacity of cathode (Ritchie et al, 1999).

Thus, mixed nickel-cobalt compounds show better properties than pure  $\text{LiCoO}_2$  and pure  $\text{LiNiO}_2$ . However, two problems need to be solved before it can be commercialised (Chowdari and Rao, 2000):

- (i) increase the thermal stability of the oxide in the charged-state (from the present value of 220°C to 260°C), and
- (ii) decrease the capacity fading on charge-discharge cycling (from the present value of 40-60% to 5-10%).

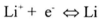
Several methods are being investigated to optimize the  $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$  batteries.

- (i) multi-doping with other metals to give composition  $\text{Li}(\text{Ni}_x\text{Co}_y\text{M}_z\text{M}'_p)\text{O}_2$
- (ii) surface coating of the cathode powder particles with other compatible oxides/non-oxides, and
- (iii) improving particle size and morphology during synthesis.

## 2.6 Thermodynamic determining factors of the positive electrode potential of Lithium Batteries (Yokokawa et al, 1998).

Lithium batteries have high voltages when lithium transition metal oxides are used as positive electrodes. The open circuit voltage depends on the transition metal in the positive electrode. These observations can be explained thermodynamically.

When  $\text{LiMO}_n$  is used as the positive electrode and lithium metal as the negative electrode, the reaction can be written as follows;

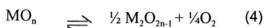
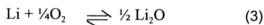


The chemical potential associated with the above electrode reaction can be written as  $\mu(\text{Li in positive electrode}) + \mu^\circ(\text{MO}_n) = \mu^\circ(\text{LiMO}_n)$  (1)

$$\{\mu(\text{Li}) - \mu^\circ(\text{Li})\} = \Delta_f G^\circ(\text{LiMO}_n) - \Delta_f G^\circ(\text{MO}_n) \quad (2)$$

Gibbs energy change for formation of  $\text{LiMO}_n$  and  $\text{MO}_n$  can be calculated from OCV values. However, it is difficult to interpret directly the difference in Gibbs energy change appearing in equation (2) due to changes in valency of the transition metals ions. To simplify interpretation, the intermediate states  $\text{Li}_2\text{O}$  and  $\text{M}_2\text{O}_{2n-1}$  are

inserted. The formation of  $\text{LiMO}_n$  from  $\text{Li} + \text{MO}_n$  can be represented by the following equations :



The above three chemical reactions can be explained as follows; that is, oxidation of Li, reduction of  $\text{MO}_n$  and the formation of a double oxide from its constituent oxides.

The valence stability,  $\Delta [\text{M}^{2n+}; \text{M}^{(2n-1)+}]$  of the transition metal oxides, and stabilization energy of a double oxide,  $\delta (\text{LiMO}_n)$  can be rewritten in equation (2) as follows;

$$\begin{aligned} \{\mu (\text{Li}) - \beta (\text{Li})\} &= \Delta [\text{Li}^0; \text{Li}^{1+}] \\ &\quad - \Delta [\text{M}^{(2n-1)+}; \text{M}^{2n+}] \\ &\quad + \delta (\text{LiMO}_n) \end{aligned} \quad (6)$$

The three terms in the right hand side correspond to the three reactions given in equations (3) - (5). Since the first term is the same in any electrode, the chemical potential is dependent on the stabilization energy of the double oxide from the constituent oxide and the valence stability of lithium and the transition metals, in other words, the redox term.

### 2.8.1 The thermodynamic determining factors in the ternary Li-M-O system

For Li-M-O positive electrode, it can be seen from table 2.4, the stabilisation energy range does not make any significant contribution to increase the potential. Where as, the redox term of the transition metal oxide is crucial in explaining changes in OCV among the various transition metals with different valence as shown in figure 2.11. This explains why  $\text{LiCoO}_2$  or  $\text{LiNiO}_2$  have large potentials.

Table 2.4: The Gibbs energy change for formation from elements and the stabilization energy of lithium transition metal double oxide at 310K (Yokokawawa et al, 1998).

$\text{LiM}_m\text{O}_n$	$\Delta G_0(\text{LiM}_m\text{O}_n)$ kJ/mol	$\delta(\text{LiM}_m\text{O}_n)$ kJ/mol	$\delta(\text{LiM}_m\text{O}_n)/F$ V	Remarks
$\text{LiVO}_2$	-875.85	-26.125	0.271	
$\text{LiCrO}_2$	-871.45	-62.168	0.644	
$\text{LiMnO}_2$	-792.85	-72.053	0.747	2.6 V
$\text{LiFeO}_2$	-694.16	-42.824	0.444	
$\text{LiCoO}_2$	-619.65			3.9 V
$\text{LiNiO}_2$	-514.96			
$\text{LiNbO}_2$	-911.36	-71.550	0.742	
$\text{LiTi}_2\text{O}_4$	-1962.4	-75.9	0.787	
$\text{LiMn}_2\text{O}_4$	-1315.61	-129.98	1.347	4.0 V
$0.5 \text{Li}_2\text{ZrO}_3$	-824.4	-22.693	0.235	
$0.5 \text{Li}_2\text{HfO}_3$	-854.51	-30.099	0.312	
$\text{LiVO}_3$	-1083.60	-93.718	0.971	
$\text{LiNbO}_3$	-1278.67	-115.546	1.198	
$\text{LiTaO}_3$	-1332.75	-97.03	1.006	
$1/3\text{Li}_3\text{VO}_4$	-586.36	-69.301	0.715	
$1/3 \text{Li}_3\text{NbO}_4$	-644.29	-69.467	0.720	
$0.5\text{Li}_2\text{CrO}_4$	-642.38	-105.882	1.097	
$0.5\text{Li}_2\text{MoO}_4$	-704.46	-90.225	0.935	
$0.5 \text{Li}_2\text{WO}_4$	-745.26	-82.971	0.860	
$0.5\text{Li}_2\text{Mo}_2\text{O}_7$	-1048.54	-100.558	1.0422	

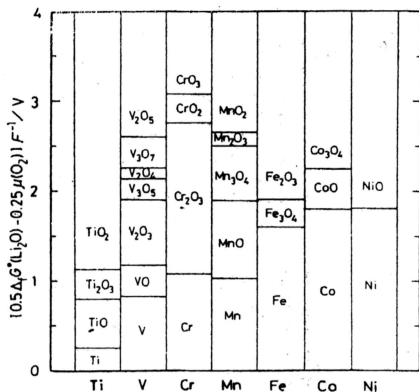


Figure 2.11: The redox equilibria in the transition metal oxides which can be directly compared with the positive electrode potential (Yokokawa et al, 1998).



## 2.9 Soft Chemistry Synthesis of $\text{LiMO}_2$

Usually lithium metal oxides are prepared based on high temperature solid-state reactions (Obrovac et al, 1998). However, for commercial purposes, it is important temperature of synthesis is low as possible to produce bulk quantities of materials. Besides, products obtained by conventional solid state reaction, at high temperatures do not ensure a high level homogeneity in the final composition, nor enough purity, nor do they allow control of morphology or microstructure. In contrast, the low-techniques, referred to as “soft chemistry”, produce more homogenous, pure, and more reproducible phases, with a morphology and microstructure that can be controlled (Prabaharan et al, 1998). Recently, several new techniques of preparation at low temperature has been developed such as sol-gel, precipitation, hydrothermal process and Pechini process (Tenakoon et al, 1997; Makamura and Kajiyama, 1999).

Among all the technique the sol-gel process has been popular. This technique is based on the polymerization of molecular precursors via wet chemical methods. One of the advantages of this process is by controlling the chemistry, one can prepare oxides in a variety of forms (powders, films, fibers, bulk monoliths) with tailored microstructures; from fully dense materials to high porous, high surface area aerogels with <1% solids (Dunn et al, 1994). In this way the sol-gel approach provides some interesting morphology for electrochemical materials where properties of surfaces and interfaces dominate the electrochemical behaviour.

The sol-gel process has generally four main stages:

- forming a solution
- gelation
- drying and
- densification.

For synthesizing lithiated transition metal oxide a modified route called particulate sol-gel approach has been developed this is because the application of true sol-gel process is quite difficult owing to the insolubility of the polymeric alcoxides. The particulate sol-gel approach is based on using metal carboxylates undergoing partial or complete hydrolysis in a mixture of aqueous or non-aqueous solvents. The generated molecular oligomers then either undergo condensation in solution to form polymeric precursors or remain as oligomers trapped in the solvent phase leading to the formation of a gel (Chang et al, 1998). Extraction of the solvent from the gel containing single or connected oligomers produces a xerogel. The particulate sol-gel process offers all the advantages and characteristics of the sol-gel process, except without the use of the unstable and expensive metal alcoxides. The figure 2.12 below shows the synthesis procedures to obtain dry vanadium and manganese oxides to be used as cathodes in lithium batteries (Owens et al, 1999).

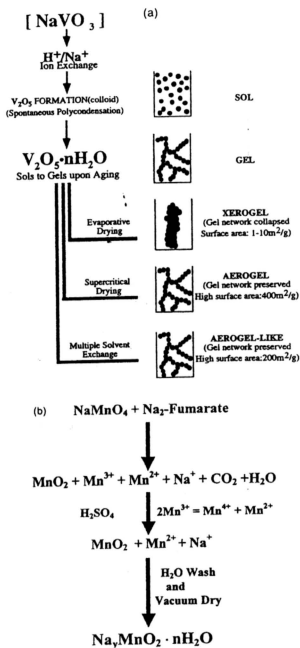


Figure 2.12: Synthesis procedures of (a) vanadium oxide (a) and manganese oxide cathodes (Owens et al, 1999).