CHAPTER 2

LITERATURE REVIEW
2.1 Electrochemistry

The subject of electrochemistry is the interrelations between electrical and chemical phenomena and in a more restricted sense, electrochemistry means the study of solutions of electrolytes and the phenomena occurring at electrodes immersed in such solution (Moore, 1955). In other words, electrochemistry discusses electrical properties of ionic solutions (Noggle, 1996). Electrochemistry takes place by diffusion of ions to the electrode. The electrode can act as the only source of electron transfer to or from the species solution,

\[ \text{O + ne} \quad \rightarrow \quad \text{R} \]

Here O and R are oxidised and reduced species respectively. Alternatively, it can take part in the electrode reaction as in dissolution of a metal (Alias, 2000).
2.2 Application of electrochemistry

Electrochemical reactions have many applications and these include electrolysis, electrolysise and batteries. An electrochemical reaction which takes place in an electrochemical cell can serve as a source of electrical power and examples of these power sources are the batteries.

2.3 Batteries

Batteries are devices, which convert chemical energy into electrical energy by means of an electrochemical reaction of the chemical materials stored within the devices. Batteries can act as power sources.

2.3.1 Basic components of batteries

Batteries consist of two electrodes, an anode and a cathode. The other component of a battery is the electrolyte as shown in Figure 1 (Moore, 1983).

A redox reaction takes place between the anode and cathode species, oxidation-taking place at the anode and reduction taking place at the
cathode. The ions involved in the cell reaction travel through the electrolyte whereas the electrons take a different pathway through an external circuit.

![Diagram of a battery](image)

**Figure 2.1. Basic components of battery (Moore, 1955).**

By doing so, current is produced which can do work (Linford, 1991).

The three basic components of a battery are as follows:

1. The anode i.e. the negative electrode is the electrode where oxidation occurs and where electrons are given out to the external circuit

   \[
   M (s) \rightarrow M^{n+} (aq) + ne
   \]
2. The cathode i.e. the positive electrode is the electrode where reduction occurs and where electrons are accepted from the external circuit.

\[ \text{X}^{n+} \text{(aq)} + \text{ne} \rightarrow \text{X(s)} \]

The overall cell reaction is

\[ \text{M(s)} + \text{X}^{n+} \text{(aq)} \rightarrow \text{M}^{n+} \text{(aq)} + \text{X(s)} \]

3. The electrolyte is the ionic conductor, which provides the medium for the transfer of ions inside the cell between the anode and the cathode.

2.4 Criteria for choosing electrodes and electrolyte materials

Battery performance characteristics depends on the choice of anode, cathode and electrolyte materials. Some of the criteria for choosing anode, cathode and electrolyte are given in table 2.1 (Megahead and Ebner, 1995, Sarma and Radhakrishna, 1991).

Beck and Ruetschi (2000) proposed the ‘three E’ criteria for the success of a battery system.
Energy-high energy content with respect to unit weight and volume.

Economics-low manufacturing costs, low maintenance during use and long service life.

Environment-free of toxic materials, safe, low energy consumption during manufacture and use, long service life, high reliability and easy to recycle.

Table 2.1. Criteria for choosing anode, cathode and electrolyte

<table>
<thead>
<tr>
<th>Anode</th>
<th>Cathode</th>
<th>Electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>High electronic conductivity</td>
<td>High electronic conductivity</td>
<td>Low electronic conductivity (to avoid the self discharge of the cell)</td>
</tr>
<tr>
<td>Low ionic conductivity</td>
<td>Low ionic conductivity</td>
<td>High ionic conductivity</td>
</tr>
<tr>
<td>Stable (do not react with electrolyte)</td>
<td>Stable (do not react with electrolyte)</td>
<td>Should be compatible physically and chemically with the electrodes stable under ambient conditions</td>
</tr>
<tr>
<td>Highly electropositive (good oxidising agent)</td>
<td>Highly electronegative (good reducing agent)</td>
<td></td>
</tr>
</tbody>
</table>
According to Tsutomu Ohzuku (1997) in designing lithium ion batteries, the following 20 behaviours must be considered from the beginning of the research.

1. High specific capacity in both Ah/cm\(^2\) and Ah/g,
2. High operating for positive electrode materials,
3. Low operating voltage for negative,
4. Excellent rechargeability,
5. Easy to connect batteries in series and/or parallel,
6. High rate capability on discharge,
7. Quick charging capability,
8. Resistance against overcharging,
9. Capacity recovery even after (over) discharging to zero volt,
10. Safe, stable, reliable cell chemistry in closed cells,
11. Long cycle life,
12. Low self-discharge rate even at high temperature,
13. Low internal cell resistance capable of high-rate discharge and charge,
14. Low cell temperature even at high rate,
15. Low materials cost,
16. State-of-charge indication capability,
17. Prediction of cycle life remained,
18. Prediction, forewarning of eventual cell failure,
19. Toxicity of materials (environmental friendliness), and
20. Recyclability of materials in battery waste.

2.5 Charge/discharge processes

Although secondary batteries are rechargeable, most are not fully reversible. The amount of charge obtained during the first discharge usually cannot be fully replaced during their recharging process. Less charge is obtained during the second discharge. Their charge / discharge process is called a cycle. The reduction of charge obtainable in second and subsequent cycle is referred to as a loss of capacity (Linford, 1991).

Ideally the discharge of the battery proceeds at the theoretical voltage until the active materials are consumed and the capacity is fully utilized. The voltage then drops to zero but under actual conditions this does not happen due to increase in cell resistance and the resultant IR drop. The actual discharge curve is represented by curve 1 and curve 2. Figure 2.2 shows the characteristic discharge curves (Linden, 1994).
Figure 2.2  Characteristic discharge curves (Linden, 1994)

Figure 2.3 shows a typical multiple charge/discharge of a typical lithium-ion cell (Prabaharan and Radhakrishna, 1997).

Figure 2.3. A typical multiple charge/discharge lithium-ion cell

(Prabaharan and Radhakrishna, 1997)
For secondary batteries the polarity of the electrodes + or -, stays the same whether the battery is under charge or discharge conditions but since reversing the cell reaction involves changing on oxidation process into a reduction process and vice versa, the positions of anode and cathode are exchanged as shown in Table 2.2 (Linford, 1991).

**Table 2.2. Polarity and cathode electrodes during charge or discharge process**

<table>
<thead>
<tr>
<th></th>
<th>charge</th>
<th>discharge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Cathode</td>
<td>-</td>
<td>+</td>
</tr>
</tbody>
</table>

2.6 Types of batteries

Batteries can either be primary or secondary power sources.

2.6.1 Primary batteries (1⁰)

If the cell reaction is not reversible, the cell is called a 1⁰ battery and many primary cells are termed ‘dry cells’.
2.6.2 Types of Primary batteries

Although a number of anode – cathode combinations can be used as primary system, only a relatively few have achieved practical success.

Examples of primary batteries are:

a. Zinc – carbon or (Leclanche) dry cell which has existed for over 100 years, (McComsey and Felegyhazi, 1994).

b. Magnesium and aluminum cells, both magnesium and aluminum have high standard potential and are attractive candidates for use as anode materials in primary cell (Spellman et al, 1994).

c. Alkaline – manganese dioxide cells (Scarr and Hunter, 1994).

d. Mercuric oxide cells where the alkaline zinc/mercuric oxide battery is noted for its high capacity per unit volume, constant voltage output and good storage characteristics (Naylor, 1994).

e. Lithium cell (Linden, 1994).

Lithium primary batteries which are available in the market include Li/SO₂, Li/V₂O₅, Li/MnO₂, Li/FeS₂ and Li/CuO.
2.6.2 Secondary batteries ($2^0$)

If the product of the cell reaction can be decomposed into the original reactants simply by applying a sufficient voltage to the battery for long enough period of time, then the battery is called a secondary battery and is rechargeable.

2.6.3 Types of Secondary batteries

Secondary or rechargeable batteries are widely used in many applications. These secondary batteries include

a. lead-acid batteries which has been a successful article of commerce for over a century (Salkind et al, 1994),

b. nickel cadmium batteries which has memory effect (Uno Falk and Nilson, 1994),

c. nickel – Zn batteries (Klein and McLaron, 1994),

d. silver oxide batteries which is expensive and therefore cost is the limitation (Schiffer and Karpinski 1994),

e. iron electrode batteries (Jackovitz and Bayles 1994),
f. and rechargeable lithium ion batteries (Hossain, 1994).

Considerable research and development activities have been increasingly carried out world wide on the lithium ion batteries.

2.7 Why Li ion battery?

Research into lithium batteries began in the 1950’s when it was noticed that Li – metal was stable in a number of non-aqueous electrolytes such as fused salts, liquid SO₂ or organic electrolytes such as LiClO₄ in propylene carbonate (Jasinki, 1967). The commercialisation of lithium primary (non-rechargeable) batteries followed relatively quickly in the late 1960’s and 1970’s (Brandt, 1994). Lately the secondary (rechargeable) batteries have received the greatest attention. The question is, why lithium ion battery has attracted a great deal of the world’s attention. The answer lies in the features of the battery which are (Hossain, 1994),

1. High voltage, can cut down the number of batteries use
   (Li battery = 3 Ni Cad cells, up to about 4V per cell).
2. Lightest metal and has the smallest ionic radius.
3. High energy density (up to 150 Wh/kg, 300 Wh/L)
4. Highly electropositive
5. Superior shelf life (up to 5 to 10 years).
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**Literature Review**

Lithium ion battery also provides the best technology for use in electric vehicles that will help to reduce environmental pollution (Anderman, 1994). Another advantage of the lithium ion battery is that lithium batteries pose no environmental hazard since its long life rechargeable will greatly reduce the disposal problem.

The early lithium batteries used Li metal as the anode since lithium metal has the most negative redox potential. Batteries with metallic lithium are expected to have a high energy density. However it was found that lithium metal as anode will form dendrites after repeated cycles of recharging which can lead to and have led to explosions and shortening of the cycle life.

A new concept battery based on the lithium ion rocking chair mechanism was introduced in which the Li–ion rocks between the anode and cathode. Such batteries have been termed as ‘rocking chair’, ‘swing’, ‘see-saw’ and ‘shuttle cock’ in which Li⁺ ions are transferred back and forth between the anode and the cathode as the cell is cycled (Prabaharan and Radhakrishna, 1997; Ouvrard and Guyomard, 1996).
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Figure 2.4 shows a schematic diagram during charging and discharging of a lithium ion battery (Lister and Renshaw, 2000). In this type of lithium batteries intercalation compounds were used as electrode materials.

![Diagram of charging and discharging of a lithium ion battery]

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

2.8 Intercalation

Electrochemical intercalation means reversible incorporation of ions or molecules guests into substances (hosts) of layered, tunelled or another
disordered structure under the action of an electric field (Korovin, 1998). The intercalation products are called intercalates. An intercalation 'host' is a solid which can reversibly incorporate 'guest' atoms or molecules within its crystal lattice with only small structural changes (Jacob, 1999; Armand, 1979). The intercalation process involves three principal steps:

1. Diffusion or migration of solvated Li$^+$ ions.
2. Desolvation and injection of Li$^+$ ions into vacancy structure.
3. Diffusion of Li$^+$ ions into the host structure (Linden 1994)

The electrode reaction which occur in a Li/Li$_2$ (HOST) cell, where (HOST) is an intercalation cathode are (Linden, 1994)

\[ \text{YLi} \rightleftharpoons \text{YLi}^+ + \text{Ye} \quad \text{at the Li metal anode} \]
\[ \text{YLi}^+ + \text{Ye} + \text{Li}_{x+y} \text{(HOST)} \rightleftharpoons \text{Li}_{x+y} \text{(HOST)} \quad \text{at the cathode} \]

Overall reaction is

\[ \text{YLi} + \text{Li}_x \text{(HOST)} \rightleftharpoons \text{Li}_{x+y} \text{(HOST)} \]

Bruce and Saidi (1992) suggested a two step model of intercalation. This is shown in Figure 2.5. Their studies have established that intercalation into both the host occur by an adion mechanism.

In this mechanism a solvated cation in solution adjacent to the electrode loses part of its solvation sheath and becomes absorbed, thus forming an
Figure 2.5. Adion Mechanism of Intercalation (Bruce and Saidi, 1992)

adion on the electrode surface. This is accompanied by the injection of an
electron into the conduction band of the solid host. Subsequently the
partially solvated cation diffuses across the surface of the electrode until it
reaches a site at which insertion of the ion can occur, the ion loses the
remaining solvent molecules and enter yhe host lattice (Bruce and Saidi,

A number of factors have to be considered in the choice of the intercalation
compound such as reversibility of the intercalation reaction, cell voltage,
variation of the voltage with the state of charge and availability and cost of
the compound (Linden, 1994). In 1990, Sony introduced a new concept
based on a carbon (non-graphitic) anode and a LiCoO$_2$ cathode which they named ‘Li ion’ (Brousseley et al., 1999; Korovin 1998) since this time a lot of research and development has been increasingly carried out world wide and a variety of insertion compounds have been synthesized, characterized and analyzed (Brousseley et al., 1999; Korovin, 1998; Choi, 1996; Balkanski, 1991).

2.9 Cathode material

The cathode materials often suggested for lithium ion batteries are LiMO$_2$ (e.g. LiCoO$_2$ and LiNiO$_2$) compounds, lithium manganese oxides (e.g. LiMn$_2$O$_4$) and other materials. These compounds are strongly oxidizing in nature and as such reversibly intercalate lithium ions above 3V (Koksbang et al., 1996).

2.9.1 Type of cathode materials

LiMO$_2$ materials

(i) LiCoO$_2$

The layered structured lithium cobalt oxide, LiCoO$_2$ (lithium cobalt oxide) was among the first lithium insertion compounds described by Mizushima et al in 1980 (Koksbang et al., 1996; Amatucci et al., 1996) is currently the
most extensively used cathode material for rocking chair batteries. The cobalt compound used in the rocking chair battery from Sony is a relatively expensive material but it has favourable electrochemical properties.

(ii) LiNiO$_2$

The nickel compound is comparatively inexpensive but is much more difficult to synthesis than LiCoO$_2$ since it need to be prepared under strongly oxidizing conditions (Zhecheva and Stoyonova, 1993). Figure 2.6 shows a crystal structure of LiNiO$_2$.

The more suitable cathode material is LiNi$_x$Co$_{1-x}$O$_2$ since it is known to have higher capacity and lower material cost than LiCoO$_2$. It also exhibits better thermal stability and rechargeability than LiNiO$_2$ (Dong and Yang, 1998).

The challenge in cathode development for rechargeable rocking chair batteries is to produce a 4V lithium manganese oxide material (Huang and Bruce, 1994) which can be cycled many times, to deep discharge with excellent capacity retention and at relatively high current densities.
Figure 2.6. Crystal structure of LiNiO$_2$ (Korovin, 1998).
2.10 Anode materials

Due to high density and high voltage of lithium batteries, they have been studied for two decades. Although a commercial reality, lithium ion batteries are still the object of intense research with the aim of further improving the properties and characteristics of cathode, anode and electrolyte.

Research on anode materials has been going on and anode materials like lithium metal, lithium alloy, carbonaceous materials, oxides and nitrides have been used.

2.10.1 Lithium metal

The early lithium batteries used Li metal as the anode since lithium metal has the most negative redox potential

\[
\text{Li}^+ (\text{aq}) + e^{-} \rightleftharpoons \text{Li} (\text{s}) \quad E^0 = 3.0 \text{ V}
\]

It also has a large capacity of 3860 mA h g\(^{-1}\). Batteries with metallic lithium are expected to have a high energy density. However it was found that these batteries produced dendrites and can cause explosion (Shodai et
al., 1999). These dendrites shortens the cycle life and also the morphology of the lithium metal anode cannot be controlled which makes the ultimate safety of cycled cells difficult to predict.. It is therefore necessary to control the growth of dendrites and improve the cycle life. Lithium/electrolyte reactions also caused thermal instability of cells (Von Sacken et al., 1994). Since then active research has been taking place to find alternatives for the anode material.

2.10.2 Carbonaceous anodes

In the last decade, much research efforts have been focused on the search for suitable carbonaceous materials, either graphite or coke (Megahed and Scrosati, 1994) as an alternative anode for rechargeable lithium batteries. Carbon has been the most favoured host material in recent years since carbon is a low cost material with low operational voltage for the battery industry (Scrosati, 1992). The carbonaceous anode is coupled with a high voltage cathode e.g. LiCoO₂ in order to obtain a battery operating in the 3-4 V range.

Many different kinds of carbonaceous material have been developed such as graphite, coke or carbon fibre materials. Graphite and other forms of
carbon the so-called ‘soft’ anodes (Scrosati, 2000) readily intercalate lithium metal. The exact composition of these $\text{Li}_x\text{C}_6$ compounds depends on the form of the carbon, for graphite, $x = 1.0$ and in some petroleum cokes, $x$ is nearly 1.0 at room temperature. An important advantage of carbon over other host insertion compounds is that the potential is very close to that of lithium metal (Winans et al., 1995).

Graphite due to its layered structure can intercalate and deintercalate lithium ion efficiently. It can insert lithium according to the following scheme

$$\text{xLi} + 6\text{C} \rightarrow \text{Li}_x\text{C}_6$$

Graphite can intercalate one Li per six C under ambient conditions. The maximum theoretical capacity of graphite is 372 mA h g\(^{-1}\) and its volumetric capacity is 800 mA h ml\(^{-1}\). The higher the lithium content the lower is the potential of the carbon electrode. With increasing $x$, the potential approaches the value of metallic lithium, another reason for choosing carbon as the favoured host material. However during the first lithium uptake an irreversible loss of capacity occurs and this decreases performance, so there are still problems for practical use.
Consistent research effort have been carried out to obtain carbon material with greater specific capacity, faster kinetics and higher reliability. ‘Hard’ carbons i.e materials characterized by a highly disordered structure appear to deliver capacities much higher than LiC$_6$ (Dahn et al., 1995).

Other types of carbon based materials that have been characterized as new anodes in lithium ion batteries is potassium doped KC$_8$ compound. Upon anodic polarization, this electrode irreversibility deintercalates potassium, resulting in a graphite–like electrode, (Tossici et al., 1997). Another carbon based material that has been reported is graphitized meso-pitch-based carbon fiber (MCF). High capacity and high performance lithium-ion batteries have been developed with these anodes (Ohsaki 1997).

2.10.3 Lithiated metal alloy

Due to safety consideration (Brandt, 1994) lithium alloy, carbonaceous materials oxides and nitrides have replaced pure metal as the anode in lithium secondary batteries. However most of them show a capacity less than 372 mA h g$^{-1}$ (Hong Li et al., 1999). The more recent work has centered on several lithium insertion compounds that maintain a lithium
lithium activity close to unity (Scrosati, 1992), a value that is ideally suitable for a negative electrode.

The metal alloy anodes offer a much higher specific capacity than intercalated carbon. Li$_{4.4}$Sn compound for example shows a capacity of 710 mAhg$^{-1}$ versus 370 mAhg$^{-1}$ in the case of LiC$_6$ (Huggins, 1994).

The anodes based on LiAl alloy can be cycled up to 100 times, depending on the cycling conditions. With the alloying substrates, formation of dendrites can be reduced but metal alloys suffer from severe morphological changes upon cycling due to large volume changes (Day, 1971). The drastic volume change also cause progressive cracking. Therefore lithium alloy electrodes are difficult to use in practise.

2.10.4 Metal oxide Anodes

Many attempts have been carried out to accommodate the change of volume stress. This include using a metal oxide as the starting anode material rather than the pure metal. The oxides such as WO$_2$, MoO$_2$, Nb$_2$O can be intercalated and deintercalated reversibly by lithium ions (Hong Li et al., 1999). Due to several shortcomings, including low diffusion,
coefficient, high oxidation-reduction potential, low capacity and low
electronic conductivity oxides as anodes have attracted less attention
compared to carbonaceous materials.

However recently in 1994, Fuji Photo Film Co. Ltd filed a patent for
rechargeable lithium batteries in which amorphous oxides mainly based on
tin oxides or tin mono oxide were used as their anode material. Since then,
material oxides attracted much interest for use in lithium rechargeable
batteries. Morales and Sanchez stated that these new anodes have
theoretical volumetric and gravimetric, capacity advantages of four and two
time, respectively over carbon.

The best results so far have been obtained with amorphous SnO doped with
various elements (B, Al, P). SnO₂ system can accommodate more than 7
Li atoms per mole of compound suggesting that the underlying process
cannot be an intercalation reaction. A decomposition reaction initially
takes place that yields Li₂O and Sn and is followed by the fomation of a
Li – Sn alloy (Morales and Sanchez, 1999).

Courtney and Dahn (1997) suggested that the reaction of lithium with tin
oxide follows a two step processes.
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The best results so far have been obtained with amorphous SnO doped with various elements (B, A1, P). SnO₂ system can accommodate more than 7 Li atoms per mole of compound suggesting that the underlying process cannot be an intercalation reaction. A decomposition reaction initially takes place that yields Li₂O and Sn and is followed by the fomation of a Li – Sn alloy (Morales and Sanchez, 1999).

Courtney and Dahn (1997) suggested that the reaction of lithium with tin oxide follows a two step processes.
SnO + 2Li → Sn + Li₂O
Sn + 4.4Li → Li₄.₄Sn

Aggregation of tin atoms formed during the reduction process and capacity fades upon cycling. To improve cycling behaviour SnO₂ was doped with B and In. These impurities may facilitate the dispersal of the Sn atoms. Indium and boron were chosen because tin – doped indium oxide (ITO) electrodes show good performance as electrochromic materials and the favourable effect of B in tin-based composite oxides containing Sn (II)-O bonds as the active site for lithium insertion (Morales and Sanchez, 1999).

2.10.5 ‘Zero strain’ compounds

‘Zero strain’ compounds are substances that belong to group of compound with formula Li(Li₁/₃Ti₅/₃)O₄. Examples are LiTi₂O₄ and Li₄Ti₅O₁₂. The intercalation process of these compounds is as follows,

Li₄Ti₅O₁₂ + 3Li → Li₇Ti₅O₁₂

There is very little structural deformation (Scrosati, 2000) and due to this advantage zero strain electrode has good cyclability and constant potential upon cycling (Arrabito, 2000). Thus the zero strain compounds have promising features as anode material in lithium ion batteries.
2.10.6 Perovskite structure anodes

Today, research and investigations are being carried out on perovskite structure compound. The perovskite type oxides of the type ABO$_3$ example BaPbO$_3$ (barium metaplumbate) are conductive ceramic at room temperature and also a superconductor at low temperature. The crystal structure of BaPbO$_3$ is an orthorhombic perovskite. Figure 2.7 shows the perovskite structure (Zhong et al., 2000).

![Perovskite structure diagram](image)

Figure 2.7. Schematic illustration of the perovskite structure of BaPbO$_3$ (Zhong et al., 2000)
2.10.7 Other types of anode material

Recent anode material that have been reported include

a. CaSi$_2$—a new inorganic anode material which shows promising reversible behaviour over extended cycles (Prabaharan et al., 2000),

b. Novel SnS$_2$—both amorphous SnS$_2$ and crystalline SnS$_2$ were revealed as promising candidates for the rechargeable lithium battery anode (Momma et al., 2000),

c. Amorphous Sn – Ca alloy - Sn-Ca system was selected due to the fact that calcium has very high elastic modulus than other elements like Cu, Fe etc and it can absorb large mechanical strain and stress during the cycles of charge and discharge (Fang and Chowdari, 2000)

d. Novel tin oxide (Connor and Irvine 2000)

e. Nanocrystalline Mg$_2$Sn (Kim et al., 2000)

f. Modified graphite – where the surface is covered with high polymer to form a thick carbonized film which improve the characteristics of intercalation/deintercalation (Shuting et al., 2000).
In 2001, tin and tin based intermetallic compounds (Wachtler et al., 2001) and Sn-Ni compounds (Crosnier et al., 2001) have been tested as anodes for lithium ion batteries.

It can be seen from the above reported anodes that one of the material which has potential as future anode are the sulphides based compounds.

2.11 What are sulphides?

Sulphide is a type of salt. Metals and non metals will combine with sulphur to form sulphides.

2.11.1 Types of sulphides

a. ionic sulphides

Only the sulphides of the s-block metals are essentially ionic e.g. Li₂S, Na₂S and K₂S. The sulphides of the S – block metals are readily soluble giving alkaline solution (Liptrot , 1983)

\[ S^{2-} + H_2O(l) \rightarrow HS^- + OH^- (aq) \]
Hydrolysis of the $S^{2-}$ ion is incomplete in cold water but goes to completion on boiling, for hydrogen sulphide gas is evolved.

$$
\text{HS}^{2-} + \text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{S (g)} + \text{OH}^- \text{ (aq)}
$$

The ionic sulphides react with sulphur on heating to form polysulphides containing $S_x^{2-}$ ions chains of sulphur atom in the ions (Brown, 1986).

$$
S^{2-} \text{ (aq)} + (x-1) \text{S(s)} \rightarrow S_x^{2-} \text{ (aq)}
$$

b. Covalent Sulphides

The greatest proportion of metallic sulphides are covalent and they are insoluble in water. Many of them according to Bandtock and Hanson (1974) occur naturally and are highly coloured with a metallic lustre e.g. ZnS (whitish), PbS (black) etc.

c. Transition metal sulphides

Transition metal sulphides behave very much like alloys and many show metallic properties e.g. metallic lustre and conductivity. Generally they cannot be allocated definite formulae i.e they may be non stoichiometric, the composition of iron(II) sulphide for instance, varies, between Fe_{0.86}S and Fe_{0.89}S (Liptrot, 1983).
2.11.2 Sulphides as semiconductor

Solid state materials can be grouped into three classes – insulators, semiconductors and conductors. Semiconductors have conductivities between those of insulators and those of conductors (~$10^{-8}$ to $10^2$ S cm$^{-1}$). The conductivity of a semiconductor is generally sensitive to temperature, illumination, magnetic field and minute amount of impurity atoms. This sensitivity in conductivity makes the semiconductor one of the most important materials for electronic applications.

Semiconductors are classified into two major groups namely elemental semiconductors such as Si and Ge in Group IV and compound semiconductors which are formed by the combination of Group III and Group V elements and Group IV and Group VI elements.

The sulphides semiconductors e.g PbS and SnS belong to the compound semiconductors which are composed of the Group IV and Group VI elements. Table 2.3 shows some examples of element and compound semiconductors (Sze, 1985).
Table 2.3. Element and compound semiconductors

<table>
<thead>
<tr>
<th>Element</th>
<th>IV – IV Compounds</th>
<th>III – V Compounds</th>
<th>II – VI Compounds</th>
<th>IV – VI Compounds</th>
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<td>Si</td>
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<td>AlAs</td>
<td>CdS</td>
<td>PbS</td>
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2.11.3 Properties of PbS and SnS

<table>
<thead>
<tr>
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<th>SnS</th>
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<tr>
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<td>Melting point</td>
<td>1118°C</td>
<td>880°C</td>
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<td>Colour</td>
<td>Grey or silver</td>
<td>Brown black / grey</td>
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<td>Appearance</td>
<td>Crystalline solid</td>
<td>Crystalline solid</td>
</tr>
</tbody>
</table>
Structure of PbS and SnS are shown below (Wells, 1975)

**Structure of PbS**

![Lead(II) sulfide](image)

**Structure of SnS**

![Tin(II) sulfide](image)
2.11.4 Preparation method of metallic sulphides

Sodium, potassium and ammonium sulphides are soluble in water and can be prepared from hydrogen sulphide and the corresponding alkali or by direct combination (Holmyard, 1956).

a) double decomposition

This method is suitable for both, either soluble or insoluble sulphides. In this method, hydrogen sulphide gas is bubbled through a solution of the appropriate metal salt

\[
\text{e.g. } \text{CuSO}_4 (aq) + \text{H}_2\text{S(g)} \rightarrow \text{CuS(s)} + \text{H}_2\text{SO}_4 (aq)
\]

In case where the sulphides are soluble in the acid produced by the reaction, ammonia solution must be added to neutralise the acid and increase the yield. Zinc sulphide and iron (II) sulphide fall into this category (Barker and Knapp, 1978).

b) direct combination

Sulphides can be prepared by direct combination of the metal and sulphur.
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The metal and sulphur are heated until reaction occurs (Barker and Knapp, 1978).

\[ \text{e.g. } \text{Zn(s)} + \text{S(s)} \rightarrow \text{ZnS(s)} + \text{heat} \]

c) By precipitation

A sulphide salt is reacted with the appropriate metal salt in a reaction vessel until a precipitate appears.

\[ \text{e.g. } \text{Na}_2\text{S(aq)} + \text{SnCl}_2 \text{ (aq)} \rightarrow \text{NaCl (aq)} + \text{SnS (s)} \]

Since NaCl is soluble, therefore SnS can be removed from the mixture by filtration. This method is less hazardous than the method with hydrogen sulphide gas.

d) Chemical bath deposition

Sulphides is obtained by reacting the appropriate metal salt with thiourea in a reaction vessel. The sulphide is deposited on a substrate. This method has been used successfully to prepare Cd\textsubscript{x}Pb\textsubscript{1-x}S films. (Upadhaya, Chandra, 1994).
Intensive research and investigations for lithium batteries components are still going on in an effort to obtain the high density rechargeable batteries. While energy density is obviously an important features, other issues like safety, reliability, robustness to abuse, cost and cycle life are also essential.