CHAPTER 1

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1.1 Background

The recent boom in portable electronics equipment such as laptops computers, smart cards and video cameras has fueled the interest in battery research. The battery, which has attracted a great deal of worldwide attention, is the lithium ion battery or lithium rocking chair battery. Reasons being, lithium ion battery has high voltage ($\sim 3.6 \text{ V}$), light weight and strong electropositive nature ($E^\theta = -3.05 \text{ V}$) and high specific discharge capacity i.e. 3880 mAh g $^{-1}$ (Yamamnoto et al., 1995).

With the above mentioned properties lithium ion battery can cut down the number of batteries used (one lithium battery to three nickel cadmium cells), perfect for use in small portable equipments. Commercial applications of lithium ion battery include commercial satellites, communication devices (cell phones) and laptop computers. These devices are now becoming smaller, lighter, multifunctional and useful for consumers. However for cellular phone users longer "talk time" is preferred requiring batteries with higher energy densities. The energy

density of currently available batteries is insufficient to meet demands. To overcome this problem many research has been carried out and focus on the cathode and anode materials as well as electrolyte of the lithium ion battery.

The early lithium batteries are of the configuration Li/electrolyte/intercalation compounds. The Li metal is the anode and the intercalation compound is the cathode. An example is the Li/MoS₂ (Moli cell). This type of cell has caused some equipment to catch fire and explode. The cell was removed from the market as lithium intercalation compounds were produced, examples are LiNiO₂ and LiCoO₂.

The lithium anode was then replaced by carbon. Examples are natural graphite (NG 7) and petroleum coke which has a capacity of ~200 m Ah g⁻¹ that is smaller than for lithium metal (Winans et al., 1995). No dendritic materials formed. Non carbon materials have also been used as anodes in batteries. Of these the first is tin based oxides. However, the formation of tin agglomerates decreases the battery capacity upon cycling (Courtney and Dahn, 1997; Kim 2000)

Sony has used LiCoO2, as the cathode material and C as the anode material

in their commercialized batteries. So far LiCoO2 gives the highest energy compared to other lithiated transition oxide compounds. Another anode candidate is barium metaplumbate, a perovskite structure compound (Zhong et al., 2000). It is thought that perovskite structure compounds can intercalate and deintercalate lithium ions easily during the charging and discharging processes and thus has the potential to be a favourable anode material but barium metaplumbate does not exist as a single phase.

Other anode candidate that have been reported include Ni-Sn alloys (Ehrlich et al., 2000), nanocrystalline Mg₂Sn which maintains a capacity between 660 to 450 mA h g⁻¹ during the first 10 cycles (Kim et al., 2000), Al/Al₂O₃ composites (Jeong et al., 2000) and CaSi₂ which exhibits similar charge trends of a carbon based Li/C₆ system (Prabaharan et al., 2000).

Crystalline SnS_2 and amorphous SnS_2 which show a high capacity of 600 mAhg $^{-1}$ and ~ 300 mAhg $^{-1}$ at initial stage respectively are also promising anode candidates for lithium ion battery (Momma et al., 2000). Another possible anode material is Sn-Ca alloy which has a capacity of about 400 mA h g $^{-1}$ and retains 62 % of the capacity after 60 cycles (Fang and Chowdari, 2000).

1.2 Why metallic sulphides as anode material?

Some of the materials used as anodes electrode have a perovskite structure (e.g. BaPbO₃) which is a common property of superconductors. Others such as Sn-Ca, Mg₂Sn and CaSi₂ are II-IV compounds. Since perovskite structures and II-IV compounds can behave as anode material in Li-ion batteries, it is thought that metallic sulphides semiconducting materials example PbS and SnS would exhibit similar properties for anode materials. Moreover SnS has a layer structure which resembles graphite (Barnett and Wilson, 1960). Studies also show that sulphides have been used as cathode. An example of this is amorphous molybdenum trisulphide which was prepared by passing hydrogen sulphide through a solution of ammonium paramolybdate in aqueous ammonia for four hours (Jacobson et al., 1979).

1.3 Objectives of the present work

The objective of the present work is to prepare sulphides based anode materials namely PbS and SnS. PbS is prepared by the chemical bath deposition technique. In this preparation equal volume of 1M lead nitrate (PbNO₃) and thiourea [(NH₂)₂CS] were stirred in a reaction vessel. This technique is simple and inexpensive.

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SnS will be prepared by the double decomposition technique whereby hydrogen sulphide gas is passed through a solution of stannous salt.

The samples prepared will be characterized by X-ray diffraction to confirm the identity of the product. Energy dispersive analysis of X-ray (EDAX) is also carried out to determine the elemental composition of the sample and thereby confirmation of the material's identity.

The samples prepared will be subjected to cyclic voltammetry in order to determine its intercalating/deintercalating properties and hence its ability as an anode material.