CHAPTER 1

Introduction

1.1. Introduction

The recent rapid development in technology has led to the urgent need of an innovative and more efficient power sources. This has prompted active research on electrochemical power sources to replace the conventional batteries with a high energy density, long-life, environmentally friendly, low cost batteries. Batteries based on the combination of a lithium metal (or of a lithiated carbon) anode and a lithium intercalation cathode, have in principle, the requisites to meet these requirements (Scrosati, 2000). These batteries were first commercialised by Sony in June 1991 and they are known as lithium ion batteries, which are based on rocking chair concept (Guyomard and Tarascon, 1994).

High energy density rechargeable lithium ion batteries are now successfully replacing nickel-metal hydride for use in portable electronic devices like notebook PC, camcorders and cellular phones. Polymer Li-ion batteries which uses gel or polymer as electrolyte are extensively used in mobile phones due to design flexibility, leak- free and improved safety. The present world production of Li-ion cells is around 400 M/year with a market value of US $2.5 billion and the demand is expected to grow at annual rate of 35-40% till the year 2005 (Chowdari and Rao, 2000). Efforts are underway to scale up use in a number of military and commercial applications, including underwater propulsion and electric vehicles.

However, the present-day Li-ion batteries are expensive. Intense research is carried out with the aim of reducing cost and improving their performance and safety aspects. Expected advancements in the lithium ion technology include (Scrosati, 2000):

- The replacement of carbonaceous materials with alternative low-voltage, Li-accepting anode compounds, with the aim of improving safety characteristics.
- the replacement of cobalt with nickel or manganese in the cathode structure, with aim of reducing cost and environmental impact.
- the replacement of the liquid-like electrolyte with a plastic membrane which may act as both separator and the electrolyte, with the aim of improving battery's design and reliability.

1.2 Problems Encountered On Developing An Efficient Li-Ion Battery

In order, to develop high energy density battery, it is important to use high capacity electrode material. Lithium was the obvious choice as the anode material due to it being the lightest metal and highly electropositive. However, during charging, the deposition of "dendritic lithium" on the electrode causes the battery discharge capacity to reduce and safety hazard. To overcome these problems, it was suggested that carbon was used as anode material.

Carbon is a low cost material for battery industry. Many carbanaceous materials are available as electrode materials in lithium batteries. Graphite with different forms of a layered structure can intercalate with lithium ions to form LiC_6 with a maximum theoretical capacity of 372 $mAhg^{-1}$

$$Li + 6C \Leftrightarrow LiC_6$$

During the first electrochemical absorption of lithium ions, a passivating film forms, which allows the continuous operation of carbonaceous anode. The formation of this film is accompanied by some initial irreversible capacity resulting into the evolution of gas products, which is highly undesirable in terms of safety (Scrosati, 2000).

Lately, lithium-metal alloys have been investigated as a potential anode material, as they have a much higher specific capacity than carbonaceous material (i.e.710 mAh g^{-1}). However, drastic volume changes, which is accompanied by mechanical stress and cracks during cycling makes them difficult for practical use.

Apart from anode materials, a lot of attention had also been focused on cathode materials. $LiCoO_2$ is extensively used cathode material in commercial lithium ion batteries due to its highly favourable electrochemical properties. Its main drawbacks are cost and environmental risk. Alternative materials have been proposed $LiNiO_2$ is a possible candidate, as it offers a higher capacity but it is more difficult to synthesize than $LiCoO_2$. Considerable attention has been devoted to manganese based compounds. Manganese has the advantage of lower cost and is environmentally friendlier than cobalt or nickel. However, $LiMn_2O_4$ electrodes suffer low specific capacity and storage losses.

The choice of electrolyte is also important. Ideally it should have high ionic conductivity, induces ideal protective film over carbon anode and sustains a high operational voltage of the lithium metal oxide cathode (Scrosati, 2000). One of the first electrolytes to be used in Li-ion battery was a solution of $LiPF_6$ in propylene carbonate(PC) - diethylcarbonate (DEC) mixture. However, this mixture causes exfoliation phenomenon in carbonaceous anodes. $LiPF_6$ solutions in ethylene carbonate (EC) - dimethylcarbonate (DMC) are used in commercial Li-ions batteries. This electrolyte is favoured due to high ionic conductivity, good electrochemical stability and favours formation of uniform film graphite anode.

The most recent development in lithium ion batteries is to use solid polymer electrolyte, which can be used as both the separator and electrolyte. Solid polymer electrolyte offers the advantages of a "nonliquid" battery, flexibility of designing thin batteries in a variety of configuration and safety. Main drawback is poor ionic conductivity compared to organic electrolyte. Another class of polymer electrolytes called gel electrolytes has been developed. They have a higher conductivity but are less chemically stable than solid polymer electrolyte.

Inorganic liquid electrolyte of $LiAlCl_4$ in SO_2 are an attractive choice electrolyte as they have the highest ionic conductivity, for lithium ion batteries. However, safety is of concern.

Researches on cathode, anode and solid electrolytes are actively being pursued to achieve a highly efficient and safe Li-ion battery.

1.3 Objective of this research

The need for more efficient power sources with the advancement of technology has fueled a strong interest in lithium ion batteries. The advantages of the Li-ion battery concept over current battery technologies are numerous: High gravimetric and volumetric energy density, high single cell voltage, no memory effect, and the potential to be fabricated out of all non toxic materials (Ceder and Aydinol, 1998). To build a high voltage Li-ion battery, the materials for the positive or negative electrode should be chosen in the high or low potential range respectively.

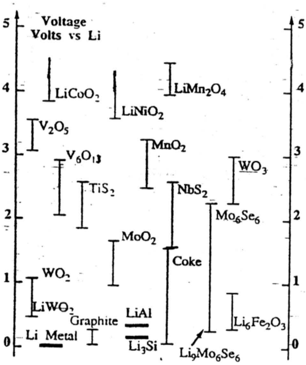

Figure 1.1: The range of intercalation potentials for various materials (Guyomard and Tarascon, 1994).

From figure1.1, it can be clearly seen that $LiCoO_2$ and $LiNiO_2$ are suitable cathode materials to produce high voltage Li-ion batteries.

The main objective of this research is to synthesize cathode materials, which have the advantages of $LiCoO_2$ and $LiNiO_2$. The cathode material will be prepared using "soft chemistry" sol-gel technique. The materials prepared in this study will be $LiCoO_2$, $LiCo_{0.2}Ni_{0.8}O_2$, $LiCo_{0.4}Ni_{0.6}O_2$ and $LiNiO_2$ using tartaric as a chelating agent. Fourier Transform Infrared Spectroscopy will be carried out on the precursors heated at 400°C and 800°C to ensure that impurities such as tartrates and carbonates are removed during calcinations. The crystalline phase of the samples will be confirmed by X-ray diffraction. Cyclic voltammetry will be used to check if intercalation and de-intercalation of lithium ions occurs in the prepared samples materials. A battery will be assembled using the prepared sample material with the highest crystallinity and purity. The performance of the fabricated battery will be evaluated by galvanostatically charging and discharging at constant current, at room temperature.