

CHAPTER 1

INTRODUCTION

1.0 Introduction

It has been more than a sesqui-centenary since electrical conduction in nonmetallic solids was observed by Faraday. Solid State Ionics, coined by the late Professor Takehilo Takahashi in the early seventies has become an intriguing field of research in materials science and technology. Solid State Ionics deals with solids that display a high level of room temperature ionic conductivity as compared to liquid electrolytes. These solid electrolytes also known as fast ionic conductors because their conductivity is well above the normal ionic conductivity and is due to ions and not electrons. Many publications (Chowdari and Radhakrishna, 1988; Chowdari, Liu and Chen, 1990; Linford, 1911; Chowdari et al., 1994; Owen, 1989; Scrosati, 1994; Radhakrishna and Daud, 1991) have discussed in great detail the practical and theoretical aspects of such high conductivity including the strengths, advantages and applications of fast ionic conducting materials.

1.1 History of Lithium Batteries Development

Lithium is the most suitable material for high energy density batteries because of its low equivalent weight and high standard potential. Lithium battery research began in the 1950s when it was observed that Li-metal was stable in a number of non-aqueous electrolytes such as fused salts, liquid SO_2 or organic electrolytes such as propylene carbonate. This stability was attributed to the formation of a passivation layer that prevents the direct chemical reaction between lithium metal and the electrolyte but still

allows for lithium to go into solution during cell discharge. The commercialization of lithium primary batteries followed relatively quickly in the late 1960s and 1970s. Some of the room temperature systems that are still being manufactured today are Lithium/Sulfur dioxide (Li/SO_2) cells, lithium/manganese oxide (Li/MnO_2), lithium/polycarbon monofluoride ($\text{Li}/(\text{CF}_x)_n$) and lithium/iodine-polyvinylpyridine ($\text{Li}/\text{I}(\text{PVP})$) cells. These primary systems have found a variety of applications from military to medical with Li/MnO_2 being dominant in the market (Brandt, 1994).

The development of rechargeable batteries was much slower. Cycling of the metallic lithium anode in organic electrolytes showed that this anode was not completely reversible. Lithium was lost during each cycle. Metal deposited during charging could only be partially stripped during discharge due to corrosion and passivation. In the early 1970s one approach to solve this problem was to go to molten salt systems (LiCl-KCl eutectic) using Li-Al alloy anode and FeS cathode. The development of this specific high temperature system is being continued to date with stationary or electric vehicle applications in mind.

The development of room temperature rechargeable battery system received greater attention when EXXON announced its intentions to commercialize the Li/TiS_2 system in the mid 1970s as a coin cell for electronic watches. Since then, large numbers of rechargeable systems with different cathode materials, different lithium metal or lithium compound based anodes and electrolytes have been investigated and developed (Table 1.1).

Table 1.1 : Overview of the sequence of development of components and systems for rechargeable lithium batteries.[Brandt, 1994]

Year	Development of compounds			Systems
	Anode	Cathode	Electrolyte	
1970's	Lithium metal (Li) Lithium Alloys	Transition metal Sulfides (TiS ₂ , MoS ₂)	Liquid organic Electrolytes (LE)	Li/LE/TiS ₂
		Transition metal oxides (V ₂ O ₅ , V ₆ O ₁₃) Liquid Cathodes (SO ₂)	Solid inorganic Electrolytes (Li ₃ N)	Li/SO ₂
1980's	Li-intercalation (LiWO ₂)	Selenides (NbSe ₃) Discharged cathodes (LiCoO ₂ , LiNiO ₂)	Polymer electrolytes	Li/LE/MoS ₂ Li/LE/NbSe ₃ Li/LE/LiCoO ₂
	Li-carbon (LiC ₁₂) (Coke)	Manganese oxide (Li _x MnO ₂)	Plasticized polymer Electrolytes	Li/PE/V ₂ O ₅ , V ₆ O ₁₃ Li/LE/MnO ₂ C/LE/LiCoO ₂
1990's	Li-carbon (LiC ₆) (graphite)	Manganese spinels (LiMn ₂ O ₄)		C/LE/LiMn ₂ O ₄

To date, a variety of systems are being manufactured as coin cells in Japan (Brandt, 1994). These cells however have a relatively poor life cycle for high depth of discharge and are used nearly exclusively for memory back up for computers.

In 1994, Sony's lithium ion cell entered the market in commercial quantities. It was then the only rechargeable cell type. This system is being used at present to power cellular telephones, video camcorders and notebook computers (Brandt, 1994).

1.2 Recent Focus of Lithium Batteries Development

The need for a high power long-life and rechargeable power source for a large variety of portable consumer devices has requested the urgent development of a reliable high energy density, environmental friendly and safe battery systems. 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. Indeed, a first generation of lithium batteries using the rocking chair concept and generally called lithium ion batteries has achieved commercial success.

Lithium ion batteries are presently produced at a rate of several million units per month and are rapidly replacing the bulkier and less energetic nickel-cadmium and nickel-metal hydride batteries in cellular phones and computers. Although a commercial reality, lithium ion batteries are still the subject of intense research with the aim of further improving their properties and characteristics. Expected advancements in the lithium-ion technology include:

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

1.3 Project Focus

The aim of this project is to synthesize lithium intercalation compound based on the LiNiO_2 structure. As such cobalt, manganese and aluminium will be added to form lithium-nickel-cobalt-oxide, lithium-nickel-cobalt-manganese-oxide and lithium-nickel-cobalt-manganese-aluminium-oxide. The lithium mixed metal oxides will be prepared by the sol-gel technique. The precursors obtained will be subjected to Differential Scanning Calorimetry (DSC) to determine the starting temperature at which the materials will form. Knowing this, the precursors will then be heated, but at a higher temperature of 400°C , 800°C and 950°C for 5 hours. Fourier Transform Infrared Spectroscopy (FTIR) will then be needed to ensure that the acetates and hydrates have been removed during the "burning process" at the various temperatures mentioned. (In order to confirm the identification of the samples heated at 950°C , (Energy Dispersive Analysis of X-rays (EDAX) will be carried out. The starting composition and the atomic percentage of the elements provided by EDAX will be compared to justify that the samples have the same percentage of elemental ratio before and after calcination.) Cyclic voltammetry will be used to check if lithium intercalation and de-intercalation occurs within the samples and finally an electrochemical cell will be fabricated using one of the samples for confirmation of lithium intercalation and de-intercalation in a practical case.