

HUM METALS (MANGANESE, CHROMIUM, COBALT
AND NICKEL) AS CATALYSTS IN THE
POLYMERIZATION OF METHACRYLAMIDE

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ABSTRACT

Spinel LiMn_2O_4 (CA-EG mixture assisted), LiMn_2O_4 (CA assisted), LiMn_2O_4 (PA assisted), Cr-doped $\text{LiCr}_x\text{Mn}_{2-x}\text{O}_4$ and layered $\text{LiCo}_{0.7}\text{Al}_{0.3}\text{O}_2$ (CA and PA assisted) cathode materials have been synthesized by a sol-gel method using organic acid as a chelating agent. This technique offers better homogeneity, preferred surface morphology, reduced heat treatment conditions, sub-micron sized particles and better crystallinity. The dependence of the physiochemical properties of the powder materials on the various calcination temperatures and organic acid quantity have been extensively studied. Electrochemical behaviors of the prepared powder materials were analyzed using galvanostatic charge-discharge cycling studies in the voltage range 3.0-4.3 V (vs. Li metal) using 1 M LiPF_6 -EC/DMC as electrolyte. Materials LiMn_2O_4 (CA-EG mixture assisted), LiMn_2O_4 (CA assisted), LiMn_2O_4 (PA assisted), Cr-doped $\text{LiCr}_x\text{Mn}_{2-x}\text{O}_4$, $\text{LiCo}_{0.7}\text{Al}_{0.3}\text{O}_2$ (CA assisted) and $\text{LiCo}_{0.7}\text{Al}_{0.3}\text{O}_2$ (PA assisted) delivered initial discharge capacity of 29.66, 20.94, 41.65, 49.50, 97.34 and 74.43 mA h/g with the capacity retention of 71.4, 93.7, 90.6, 91.6, 90.8 and 98.4 % of its initial capacity over only 3rd cycle, respectively. Coulombic efficiency for the materials of LiMn_2O_4 (CA-EG mixture assisted), LiMn_2O_4 (CA assisted), LiMn_2O_4 (PA assisted), Cr-doped $\text{LiCr}_x\text{Mn}_{2-x}\text{O}_4$, $\text{LiCo}_{0.7}\text{Al}_{0.3}\text{O}_2$ (CA assisted) and $\text{LiCo}_{0.7}\text{Al}_{0.3}\text{O}_2$ (PA assisted) were found to be 96.2, 89.18, 74.8, 97.6, 92.8 and 94.7 % after only three cycles, respectively. Electrochemical evaluation shows that $\text{LiCo}_{0.7}\text{Al}_{0.3}\text{O}_2$ (CA assisted) materials exhibit higher initial discharge capacity whereas $\text{LiCo}_{0.7}\text{Al}_{0.3}\text{O}_2$ (PA assisted) materials exhibit a better capacity retention and good coulombic efficiency.

ABSTRAK

Bahan katod spinel LiMn_2O_4 (campuran bantuan CA-EG), LiMn_2O_4 (bantuan CA), LiMn_2O_4 (bantuan PA), $\text{LiCr}_x\text{Mn}_{2-x}\text{O}_4$ terdopkan Cr dan lapisan $\text{LiCo}_{0.7}\text{Al}_{0.3}\text{O}_2$ (bantuan CA dan PA) telah berjaya disintesis melalui teknik sol-gel menggunakan asid organik sebagai agen pengkelat. Teknik ini mampu memberikan kehomogenan yang lebih baik, kepilihan morfologi permukaan, pengurangan keadaan rawatan haba, partikel bersaiz sub-mikron dan penghabluran yang lebih baik. Pergantungan antara sifat fisiokimia bahan serbuk terhadap pelbagai suhu pengkalsinan dan kuantiti asid organik telah dikaji secara meluas. Sifat elektrokimia bahan serbuk yang telah disediakan diuji dengan kaedah kitaran cas-discas galvanostatik dengan julat voltan antara 3.0 hingga 4.3 V (terhadap logam Li) menggunakan 1 M $\text{LiPF}_6\text{-EC/DMC}$ sebagai elektrolit. Bahan LiMn_2O_4 (campuran bantuan CA-EG), LiMn_2O_4 (bantuan CA), LiMn_2O_4 (bantuan PA), $\text{LiCr}_x\text{Mn}_{2-x}\text{O}_4$ terdopkan Cr, $\text{LiCo}_{0.7}\text{Al}_{0.3}\text{O}_2$ (bantuan CA) dan $\text{LiCo}_{0.7}\text{Al}_{0.3}\text{O}_2$ (bantuan PA) menghasilkan kapasiti discas permulaan sebanyak 29.66, 20.94, 41.65, 49.50, 97.34 dan 74.43 mA h/g dengan kapasiti penahanan sebanyak 71.4, 93.7, 90.6, 91.6, 90.8 dan 98.4 % daripada kapasiti permulaan selepas kitaran ketiga. Kecekapan coulomb bagi LiMn_2O_4 (campuran bantuan CA-EG), LiMn_2O_4 (bantuan CA), LiMn_2O_4 (bantuan PA), $\text{LiCr}_x\text{Mn}_{2-x}\text{O}_4$ terdopkan Cr, $\text{LiCo}_{0.7}\text{Al}_{0.3}\text{O}_2$ (bantuan CA) dan $\text{LiCo}_{0.7}\text{Al}_{0.3}\text{O}_2$ (bantuan PA) didapati sebanyak 96.2, 89.18, 74.8, 97.6, 92.8 dan 94.7 % selepas hanya tiga kitaran. Evolusi elektrokimia menunjukkan bahawa $\text{LiCo}_{0.7}\text{Al}_{0.3}\text{O}_2$ (bantuan CA) menunjukkan kapasiti discas permulaan yang tinggi manakala $\text{LiCo}_{0.7}\text{Al}_{0.3}\text{O}_2$ (bantuan PA) menunjukkan kapasiti penahanan dan kecekapan coulomb yang lebih baik.

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LIST OF SYMBOLS

| | | |
|--------------------|---|------------------------------|
| $^{\circ}\text{C}$ | - | Degree Celsius |
| θ | - | Scattering Angle |
| μ | - | Chemical Potential |
| e | - | Charge of an Electron |
| e^{-} | - | Electron |
| g | - | Gram |
| L | - | Liter |
| m | - | Meter |
| M | - | Molar |
| mA | - | Milliampere |
| A h | - | Ampere hour |
| V | - | Voltage |
| mg | - | Milligram |
| min | - | Minute |
| A_i | - | Activity of Relevant Species |
| R | - | Gas Constant |
| T | - | Absolute Temperature |
| W h/g | - | Watt hour per gram |
| mA h/g | - | Milliampere-hour per gram |
| nm | - | Nanometer |
| E° | - | Standard Potential |
| F | - | Faraday Constant |
| ΔG° | - | Standard Free Energy |

| | | |
|------|---|--------------------|
| n | - | Number of Electron |
| Å | - | Angstrom |
| μg | - | Microgram |
| μm | - | Micrometer/Micron |
| μmol | - | Micromole |

LIST OF ABBREVIATIONS

| | | |
|--------|---|--|
| SLI | - | Starting-Lighting-Ignition |
| CA-EG | - | Citric Acid-Ethylene Glycol |
| CA | - | Citric Acid |
| EG | - | Ethylene Glycol |
| PA | - | Propionic Acid |
| PE | - | Positive Electrode |
| NE | - | Negative Electrode |
| NHE | - | Normal Hydrogen Electrode |
| PC | - | Propylene Carbonate |
| PEO | - | Polyethylene Oxide |
| EV/HEV | - | Electric Vehicles / Hybrid Electric Vehicles |
| EIS | - | Electrochemical Impedance Spectroscopy |
| EAS | - | Electro-analytical Study |
| SEI | - | Solid Electrolyte Interphase |
| CV | - | Cyclic Voltammetry |
| EC | - | Ethylene Carbonate |
| DEC | - | Diethyl Carbonate |
| TG-DTA | - | Thermogravimetry-Differential Thermal Analysis |
| BET | - | Brunauer-Emmett and Teller |
| EDAX | - | Energy Dispersive X-ray Analysis |
| XRD | - | X-ray Diffraction |
| SEM | - | Scanning Electron Microscopy |
| TEM | - | Transmission Electron Microscopy |

| | | |
|--------|---|--|
| XPS | - | X-ray Photoelectron Spectra |
| SPE | - | Solid Polymer Electrolyte |
| Ni-Cd | - | Nickel Cadmium |
| NiM-H | - | Nickel Metal-Hydride |
| ICP | - | Inductive Coupled Plasma |
| Li-ion | - | Lithium Ion |
| A cell | - | Li/1 M LiPF ₆ -EC/DMC/LiMn ₂ O ₄ (CA-EG) |
| B cell | - | Li/1 M LiPF ₆ -EC/DMC/LiMn ₂ O ₄ (CA) |
| C cell | - | Li/1 M LiPF ₆ -EC/DMC/LiMn ₂ O ₄ (PA) |
| D cell | - | Li/1 M LiPF ₆ -EC/DMC/LiCr _x Mn _{2-x} O ₄ |
| E cell | - | Li/1 M LiPF ₆ -EC/DMC/LiCo _{0.7} Al _{0.3} O ₂ (CA) |
| F cell | - | Li/1 M LiPF ₆ -EC/DMC/LiCo _{0.7} Al _{0.3} O ₂ (PA) |

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CHAPTER 1

INTRODUCTION

1.1 Historical Background of Secondary Batteries

Secondary batteries have been in existence for over 100 years. The lead-acid battery was developed in 1859 by Plante. It is still the most widely used battery, albeit with many design changes and improvements, with the automotive SLI battery by far the dominant one. The nickel-iron alkaline battery was introduced by Edison in 1908 as a power source for the early, but short-lived, electric automobile. The pocket-plate nickel-cadmium battery has been manufactured since 1909 and was used primarily for heavy-duty industrial applications. As with the primary battery systems, significant performance improvements have been made with the older secondary battery systems, and a number of newer types, such as the silver-zinc, the nickel-zinc, the hydrogen, lithium, and halogen batteries, and the high temperature systems, have been introduced into commercial use or serious development (Linden, 1994).

1.1.1 Definition of Battery

A battery is a device that converts chemical energy contained in its active materials to electric energy by means of spatially separated electrochemical oxidation and reduction reactions. The overall (redox) reaction occurs by electron

transfer from negative electrode material to positive electrode material through an external electrical circuit. In a non-electrochemical redox reaction, such as rusting or burning, the transfer of electrons occurs locally and chemical energy is converted to heat only. Although the terms “cell and battery” are often used interchangeably, the basic electrochemical reactor is the “cell” consisting of a single set of positive and negative electrodes.

Batteries can be divided into primary (non-rechargeable) and secondary (rechargeable) batteries according to the capability of electrical regeneration after chemical energy has been converted fully to electrical energy during discharge. Primary batteries cannot be recharged, i.e. the electrochemical reaction cannot be reversed. Hence, they are discharged once and discarded or recycled chemically. Nevertheless primary batteries have found many applications due to shelf life, high energy density at low to moderate discharge rate, compactness, and ease of use. Secondary batteries, also referred to as rechargeable batteries, are systems in which the electrochemical reaction can be reversed by passing current through the battery in the direction opposite of that of discharge. Although this is, in principle, possible for all batteries at very low rates i.e. practically useful secondary batteries are characterized by relatively high power density in charge as well as discharge, flat discharge curves, and acceptable low temperature performance. Moreover, rechargeable batteries have an advantage over primary batteries from an environmental point of view, because they are inherently being “recycled”.

1.1.2 Secondary Lithium Battery

Secondary lithium batteries have the same geometry and components as primary ones but both electrodes function as secondary lithium electrodes, for example by lithium intercalation in the electrode material on either side. Almost at the same time that primary lithium batteries were introduced, it was discovered that lithium could be inserted or intercalated reversibly in several compounds, which makes it possible to use these compounds as insertion cathodes in rechargeable lithium batteries. The choice of materials that can be used for the insertion cathode is

relatively wide. The best cathodes for secondary lithium batteries are those where bonding with lithium occurs at low energy levels and the structural modification of the active materials during lithium insertion/extraction is minimal (such insertion reactions are typical for certain 2-D lattices, in which case they are called intercalation reaction).

Table 1.1 shows characteristics of some of the compounds that have been used in lithium secondary batteries.

Table 1.1: Positive electrode materials and some of their characteristics (Hossain, 1995).

| Materials | Average voltage (V) ^a | Practical specific energy (W h/kg) | Lithium /mole | Comments |
|----------------------------------|----------------------------------|------------------------------------|---------------|---|
| MoS ₂ | 1.7 | 230 | 0.8 | Naturally occurring |
| MnO ₂ | 3.0 | 650 | 0.7 | Inexpensive |
| LiCoO ₂ | 3.7 | 500 | 0.5 | Good for lithium ion system |
| LiNiO ₂ | 3.5 | 480 | 0.5 | Good for lithium ion system |
| LiMn ₂ O ₄ | 3.8 | 450 | 0.8 | Good for lithium ion system |
| V ₆ O ₁₃ | 2.3 | 300 | 2.5 | Good for SPE system |
| V ₂ O ₅ | 2.8 | 490 | 1.2 | Good for SPE system |
| SO ₂ | 3.1 | 220 | 0.33 | Toxic electrolyte, good for pulse power application |
| CuCl ₂ | 3.3 | 660 | 1 | Toxic electrolyte, good for pulse power application |
| Polyacetylene | 3.2 | 340 | 1 | For polymer electrodes |
| Polypyrrole | 3.2 | 280 | 1 | For polymer electrodes |

^a Voltage vs. Lithium metal

During the 1970s and 80s many researchers were involved in programs to develop rechargeable batteries. However, until 1990, only small-scale rechargeable coin cells survived in the market despite their advantage over conventional systems in terms of energy density and environmental control. On the other hand, primary lithium batteries captured a significant market in various size and capacities. The major reasons for the small market share of rechargeable lithium batteries with lithium metal NE were their limited cycleability and, especially, potential safety hazards. The limited cycleability means that, although lithium metal may be plated with almost 100 % efficiency during charging in propylene carbonate (Chilton *et al.*,1965; Selim and Bro,1974), it can not be stripped (oxidized during discharge) as efficiently, particularly if stripping does not immediately follow deposition and the deposit is allowed to stand in contact with solution.

Although a lithium plate becomes less electro-strippable upon standing, it is mostly still in the form of metal (Selim and Bro, 1974). This metal layer has become electrically isolated from the substrate by ionically conducting layer, which forms due to corrosion (Li oxidation under reduction of electrolyte). Therefore, the lithium layer is effectively passivated. Passivation prevents further corrosion but the passivating film cause an increase in the internal cell resistance and release of corrosion products. Thus cycle by cycle, the morphology deteriorates and the plating (charging)-stripping (discharging) efficiency decreases. Moreover, the most deleterious effect of the (non-uniform) passivation layer is that it causes nonuniform lithium plating during the charging process, to an extent which may ultimately lead to total cell failure (due to dendritic short circuiting) or even to serious safety hazard (due to local over heating).

1.1.3 Rechargeable Lithium-ion Battery

There are four major rechargeable batteries currently in use (Abraham, 2001): the lead-acid battery (Pb-Acid), the nickel-cadmium battery (Ni-Cd), the nickel metal-hydride batteries (NiM-H) and the lithium-ion batteries (Li-ion). The lead-acid and nickel-cadmium batteries have a very long history of consumer use.

The nickel metal-hydride and lithium-ion are relatively new battery systems having come into existence in the early nineteen nineties. The first three batteries contain water-based (aqueous) electrolytes, whereas the lithium-ion battery utilizes electrolytes composed of lithium salt solutions in organic (non-aqueous) solvents. The Li-ion battery has many advantages over the three aqueous electrolyte-based systems (See Table 1.2) and these include:

- a) Two to three times higher voltage per single cell
- b) Two to five times higher specific energy, i.e., watt-hours per kilogram (W h/kg) of battery weight, and two to four times higher energy density, i.e., watt-hours per liter (W h/l) of battery volume.
- c) Low self-discharge and long shelf life, i.e, the battery does not loose a significant amount of its capacity while sitting idle on the shelf.
- d) No memory effect, i.e., the available capacity in a fully charged Li-ion battery is independent of its operational history, unlike the Ni-Cd system.
- e) Long charge-discharge cycle life. Li-ion batteries are capable of 500-1000 cycles at full depth of discharge.

Due to these advantages Li-ion batteries are increasingly becoming the battery of choice for portable consumer products such as cellular telephones and notebook computers.

Table 1.2: Characteristics of rechargeable batteries

| Attribute | Li-ion | NiM-H | Ni-Cd | Small Pb-Acid |
|-----------------------------|--------|-------|-------|---------------|
| Voltage (V) | 3.6 | 1.2 | 1.2 | 2.0 |
| Specific Energy (W h/kg) | 150 | 90 | 70 | 30 |
| Energy Density (W h/l) | 350 | 300 | 180 | 80 |
| Life Cycles | >1000 | >1000 | 1500 | 500 |

As result of the proliferation of these and other portable consumer products, the Li-ion battery business is expected to generate tens of billions of US dollars in sales in the not too distant future.

In lithium-ion batteries, the metallic lithium anode is replaced with a lithium insertion electrode consisting of carbon material. The introduction of carbon as an anode material and the development of insertion-type cathode materials have produced substantial improvements in energy density, cycleability, cost, and safety of secondary lithium batteries. In 1990 Sony Inc. introduced the first generation of lithium-ion batteries without metallic lithium (Ngaura *et al.*, 1990). The new concept and the excellent characteristics of the “lithium-ion” battery were enough to obtain worldwide attention. A very large research effort continues in this field, after the first generation of lithium-ion batteries. Table 1.3 shows some of the current lithium-ion battery makers and their product line.

Table 1.3: Commercial rechargeable Li-ion batteries available in the market (Kim, 2001)

| Manufac. | Type of cathode | Type of anode | Dimension (mm) | Capacity (mA h) |
|---------------|--|---------------|------------------------------|-----------------|
| Toshiba (A&T) | LiCoO ₂ | Graphite | Φ17×50~Φ18.3×65 | 740~1350 |
| | | Coke | 6.3×30×4.8~14.5×34×48 | 500~1600 |
| Sony | LiCoO ₂ | Hard carbon | 8.0×33.7×48.1~10.0×34.1×47.2 | 500~2800 |
| | LiNi _{0.8} Co _{0.2} O ₂ | Graphite | Φ14×42.8~Φ26.3×65.4 | |
| Sanyo | LiCoO ₂ | Graphite | Φ14×50~Φ18×65 | 580~1600 |
| | | | 19.5×48×6.1~35.1×67.3×6.5 | 320~1400 |
| Panasonic | LiCoO ₂ | Soft Carbon | Φ17×49.5~Φ18.3×64.7 | 830~1800 |
| | | Graphite | 29.8×47.5×6.4~34×49.8×10.4 | 630~1550 |
| E-One (Moli) | LiMn ₂ O ₄ | Graphite | Φ18.2×65,Φ26.0×65 | 1400~320 |
| | LiCoO ₂ | - | 8.6×34×48 | 1000 |

Manufac. = Manufacturer

As the result of that, many parts have been improved. So far, more than 10 major companies are sharing the market and more companies are expected to enter shortly, as they are still in the phase of developing and engineering.

The lithium-ion battery industry is growing fast as consumer electronic companies demand smaller and lighter energy storage device with high energy density. Many battery manufacturers are pursuing the development of lithium ion battery packs for application to electric vehicles. In 1998 Nissan and Sony Corporation released the first electric vehicle fleet model, which is powered by a lithium-ion battery (Kim, 2001). The battery pack consists of 12 modules and each module contains 8 cylindrical cells encased in a resin module. Each battery has a built-in cell controller to ensure that each cell is operating within a specific voltage range of 2.5 V and 4.2 V during cycling. Total battery pack capacity is 94 A h and voltage is 345 V.

1.2 Major Components of Cell and Battery

A battery consists of one or more of cells, connected in series or parallel, or both, depending on the desired output voltage and capacity. The cell consists of three major components as below:

a) **The cathode or positive electrode:** It is oxidizing electrode which accepts electrons from the external circuit and is reduced during the electrochemical reaction.

b) **The anode or negative electrode:** It is reducing or fuel electrode which gives up electrons to the external circuit and is oxidized during the electrochemical reaction.

c) **The electrolyte:** It is ionic conductor which provides the medium for transfer of electrons, as ions, inside the cell between the anode and cathode. The electrolyte is typically a liquid, such as water or other solvents, with dissolved salts, acids or alkalis to impart ionic conductivity.

The cathode must be an efficient oxidizing agent, be stable when in contact with the electrolyte, and have a useful working voltage. However, many of the cathode materials are metallic oxides, while other cathode materials are used for advanced battery systems giving high voltage and capacity.

In a practical system, the anode is selected with the following properties in mind: efficiency as a reducing agent, high columbic output (A h/g), good conductivity, stability, ease of fabrication, and low cost.

The electrolyte must have good ionic conductivity but not be electrically conductive, as this would cause internal short circuiting. Other important characteristics are nonreactivity with the electrode materials, little change in properties with change in temperature, safeness in handling, and low cost.

Physically the anode and cathode electrodes are electronically isolated in the cell to prevent internal short circuiting, but are surrounded by the electrolyte. In practical cell designs a separator material is used to separate the anode and cathode electrodes mechanically. The separator, however, is permeable to the electrolyte in order to maintain the desired ionic conductivity. In some cases the electrolyte is immobilized for non spill design.

1.2.1 Chemistry of Positive Electrode

The process, however, is even more complex for rechargeable batteries as the cell chemistry must be reversible and the reactions that occur during recharge affect all of the characteristics and the performance on subsequent cycling.

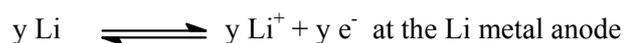
There is a relatively wide choice of materials that can be selected for the positive electrodes of lithium batteries. However, many of these, which involve reactions which break and rearrange bonds during discharge, cannot be readily reversed and are limited to primary nonrechargeable batteries. The best cathodes for

rechargeable batteries are those where there is little bonding and structural modification of the active materials during the discharge-charge reaction (Scrosati *et al.*, 1993).

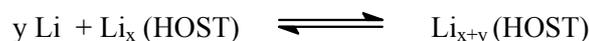
Intercalation Compounds: The insertion or intercalation compounds are among the most suitable cathode materials. In these compounds, a guest species such as lithium can be inserted interstitially into the host lattice (during discharge) and subsequently extracted during recharge with little or no structural modification of the host. The intercalation process involves three principal steps:

- a) Diffusion or migration of solvated Li^+ ions
- b) Desolvation and injection of Li^+ ions into the vacancy structure
- c) Diffusion of Li^+ ions into the host structure

The electrode reactions which occur in a $\text{Li}/\text{Li}_x(\text{HOST})$ cell, where (HOST) is an intercalation cathode, are



Leading to overall cell reaction of

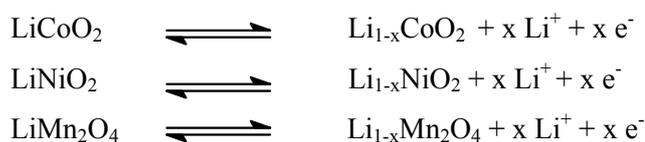


A number of factors have to be considered in the choice of the intercalation compound, such as reversibility of the intercalation reaction, cell voltage, variation of the voltage with the state of the charge, availability and cost of the compound. The key requirements for positive-electrode intercalation materials (Li_xMO_z) used in lithium cells are given below:

- 1) High free energy of reaction with lithium
- 2) Wide range of x (amount of intercalation)
- 3) Little structural change upon reaction
- 4) Highly reversible reaction
- 5) Rapid diffusion of lithium in solid
- 6) Good electronic conductivity
- 7) No solubility in electrolyte
- 8) Readily available or easily synthesized from low cost reactants

Transition metal oxides, sulfides (MoS_2 , TiS_2), and selenides (NbSe_3) are used in lithium rechargeable batteries. The LiMn_2O_4 spinel framework possesses a three

dimensional space via face sharing octahedral and tetrahedral structures, which provide conducting pathways for the insertion and extraction of lithium ions. The removal and insertion of the lithium ion for the three lithiated transition metal oxides are



The reversible value of x for LiCoO_2 and LiNiO_2 is less than or equal to 0.5, and the value is greater than or to 0.85 for lithiated manganese oxide. Thus although the theoretical capacity of LiCoO_2 and LiNiO_2 (274 mA h /g) is almost twice as high as that of LiMn_2O_4 , the reversible capacity of the three cathode materials is about the same (135 mA h/g). In the long run it is expected that the manganese-based compounds will become the material of choice as they are more abundant, less expensive, and non-toxic.

1.3 Fundamentals of Electrochemistry

Electrochemistry includes the study of chemical properties and reactions involving ions either in solution or in solids. In order to study these properties, generally electrochemical cells are constructed. Typical cell consists of two solid electrodes, the cathode and anode, in contact with an ionic conducting electrolyte. To prevent cell self-discharge, an electronically insulating material that is permeable to the working ions physically separates the electrodes. The two electrodes are put in electrical contact by an external electronically conductive wire. Two different types of electrochemical cells can be defined: electrolytic cells, and galvanic cells. In electrolytic cells an applied electrical current causes the active material to undergo decomposition; a process corresponding to the conversion of electrical energy to chemical energy. Galvanic cells, however, are capable of converting chemical energy into electrical energy. Galvanic cells generate electrical energy by the spontaneous electrode reactions that give rise to electrical current.

To understand the lithium-ion battery it is useful to consider a simple Li cell, Figure 1.1

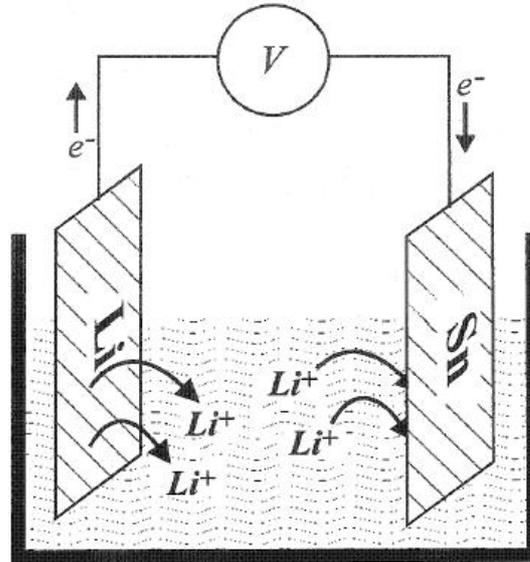


Figure 1.1: Schematic of a basic Li-Sn cell

The reaction for a cell with a negative Li-metal electrode and a positive tin (Sn) electrode is presented below. This cell is very important to the rest of the thesis, so it a good place to start. The discharge of a Li-Sn cell involves two half cell reactions. During discharge of a lithium cell, Li^+ ions are generated at the anode/electrolyte interface, and Li^+ is inserted into the cathode structure at the cathode/electrolyte interface. The electrode reactions are given below.



The full cell reaction is:



The difference in chemical potential (μ) of Li in the negative electrode compared to the positive electrode drives the reaction. The voltage difference between the electrodes is given by:

$$V = \frac{-(\mu \text{ positive} - \mu \text{ negative})}{e}$$

where e is the magnitude of the charge on an electron. To charge the cell the reaction must be reversed. Energy is required to remove Li from Sn and re-deposit it onto the negative electrode, recharging the cell. The roles of the cathode and anode are reversed when the battery is being charged.

1.3.1 Thermodynamic Background

In a cell, reactions essentially take place at two areas or sites in the device. These reaction sites are the electrodes. In generalized terms, the reaction at one electrode (reduction in the forward direction) can be represented by:



where a molecules of A take up n electrons e to form c molecules of C. At the other electrode, the reaction (oxidation in forward direction) can be represented by:



The overall reaction in the cell is given by addition of these two half cell reactions



The change in the standard free energy ΔG° of this reaction is expressed as

$$\Delta G^\circ = -nFE^\circ \quad (d)$$

where F = constant known as Faraday (96,487 C)

E° = standard electromotive force

n = number of electrons involved in stoichiometric reaction

When conditions are other than in the standard state, the voltage E of a cell is given by the Nernst equation,

$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_C^c a_D^d}{a_A^a a_B^b} \quad (e)$$

where a_i = activity of relevant species

R = gas constant

T = absolute temperature

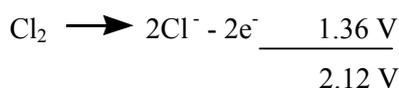
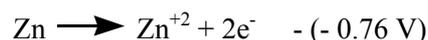
The change in the standard free energy ΔG° of a cell reaction is the driving force which enables a battery to deliver electric energy to an external circuit. The measurement of the electromotive force, incidentally, also make available data on changes in free energy, namely, entropies and enthalpies together with activity coefficients, equilibrium constants, and solubility products. Direct measurement of single (absolute) electrode potentials is considered practically impossible. To establish a scale of cell or standard potentials, a reference potential “Zero” must be established against which single electrode potentials can be measured. By convention, the standard potential of the $\text{H}_2/\text{H}^+(\text{aq})$ reaction is taken as zero and all standard potentials are referred to this potential.

1.3.1.1 Theoretical voltage

The standard potential of the cell is determined by its active materials and can be calculated from free energy data or obtained experimentally. The standard potential of a cell can also be calculated from the standard electrode potentials as follows (the oxidation potential is the negative value of the reduction potential):

Anode (oxidation potential) + cathode (reduction potential) = standard cell potential

For example, in the reaction $\text{Zn} + \text{Cl}_2 \longrightarrow \text{ZnCl}_2$



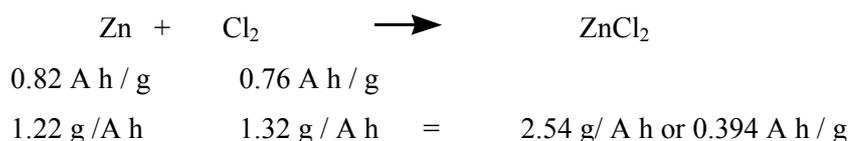
2.12 V

The cell voltage is also dependent on other factors, including concentration, temperature etc.

1.3.1.2 Theoretical capacity

The capacity of a cell is expressed as the total quantity of electricity involved in the electrochemical reaction and is defined in terms of coulombs or ampere-hours. The “ampere-hour capacity” of a battery is directly associated with the quantity of

electricity obtained from the active materials. Theoretically 1 gm-equivalent weight of material will deliver 96,487 C or 26.8 A h. (A gram-equivalent weight is the atomic or molecular weight of the active material in grams divide by the number of electrons involved in the reaction). The theoretical capacity of a battery system, based only on the active materials participating in the electrochemical reaction, is calculated from the equivalent weight of the reactants. Hence the theoretical capacity of the Zn/Cl₂ system is 0.394 A h / g, that is,



The capacity of battery is also considered on an energy (Watt hour) basis by taking the voltage as well as the quantity of electricity into consideration,

$$\text{Watt hour (W h)} = \text{voltage (V)} \times \text{ampere-hour (A h)}$$

In the Zn / Cl₂ cell example, if the standard potential is taken as 2.12 V, the theoretical watt hour capacity per gram of active material (theoretical gravimetric energy density) is Watt hour / gram capacity = 2.12 V × 0.395 A h/g = 0.838 W h /g. Similarly, the ampere-hour or watt hour capacity on a volume basis, can be calculated by using the appropriate data for ampere-hours per cubic centimeter.

1.3.1.3 Free energy

Whenever a reaction occurs, there is a decrease in the free energy of the system, which is expressed as

$$G^\circ = - nFE^\circ$$

where F = constant known as Faraday ($\approx 96,500$ C or 26.8 A h)

n = number of electrons involved in stoichiometric reaction

E[°] = standard potential, V

1.3.2 Operation of a cell

A battery consists of one or more cells, connected in series or parallel, or both, depending on the desired output voltage and capacity.

1.3.2.1 Discharge

The operation of a cell during discharge is shown schematically in the Figure 1.2

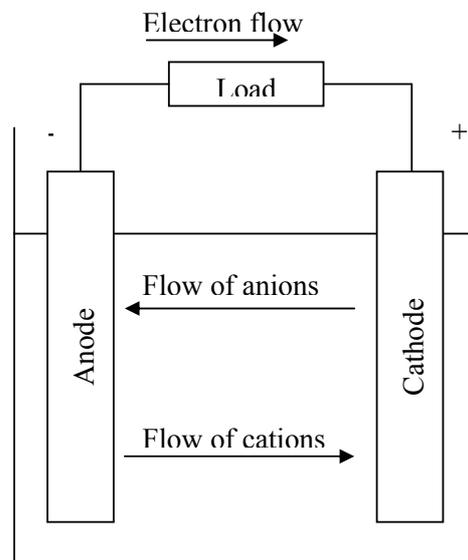
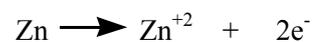


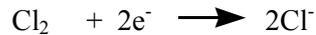
Figure 1.2: Electrochemical operation of cell (discharge)

When the cell is connected to an external load, electrons flow from the anode, which is oxidized, through the external load to the cathode, where the electrons are accepted and the cathode material is reduced. The electric circuit is completed in the electrolyte by the flow of anions (negative ions) and cations (positive ions) to the anode and cathode, respectively. The discharge reaction can be written, assuming a metal as the anode material and a cathode material such as chlorine (Cl_2), as follows

Negative electrode: anodic reaction (oxidation, loss of electrons)



Positive electrode: cathodic reaction (reduction, gain of electrons)



Overall reaction (discharge): $\text{Zn} + \text{Cl}_2 \longrightarrow \text{Zn}^{2+} + 2\text{Cl}^-$ (ZnCl_2)

1.3.2.2 Charge

During the recharge of a rechargeable or storage battery, the current flow is reversed and oxidation takes place at the positive electrode and reduction at the negative electrode, as shown in Figure 1.3. As the anode is, by definition, the electrode at which oxidation occurs and cathode the one where reduction takes place, the positive electrode is now the anode and the negative the cathode.

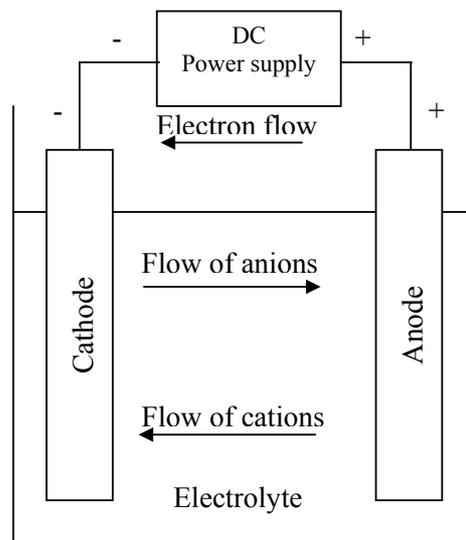


Figure 1.3: Electrochemical operation of cell (charge)

In the example of the Zn/Cl_2 cell, the reaction on charge can be written as follows:

Negative electrode: cathodic reaction (reduction, gain of electrons)



Positive electrode: anodic reaction (oxidation, loss of electrons)



Overall reaction (charge): $\text{Zn}^{2+} + 2\text{Cl}^- \longrightarrow \text{Zn} + \text{Cl}_2$

1.4 Cell Geometry

The basic cell chemistry and design are the same for all types of Li-ion batteries. Figure 1.4 shows a typical cell design. Thin layers of cathode (positive), separator, and anode (negative) are rolled up on a central mandrel and inserted into a cylindrical can. The gaps are filled with liquid electrolyte. The basic design remains unchanged on substitution of one electrode material for another, although the layer thickness might change. This is the same design used for most small commercial cells, like the 18650 (18 mm in diameter, 65 mm long) used in devices such as camcorders and laptops.

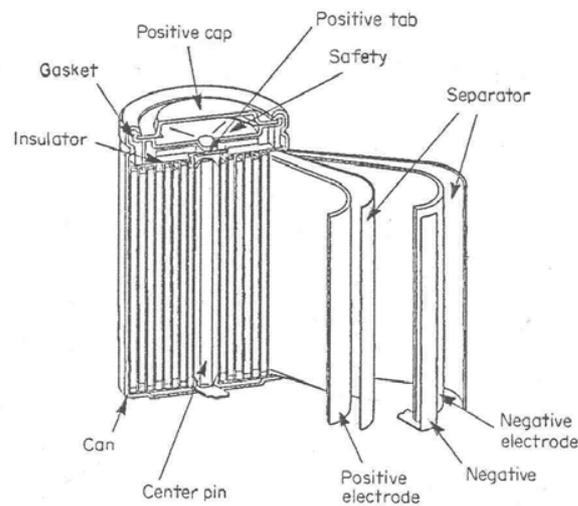


Figure 1.4: Typical design of a cylindrical 18650 cell (Beaulieu, 2002)

The lithium-ion cell can be designed in any of the typical cell constructions: flat or coin, spirally wound cylindrical, or prismatic configurations. While most of the developments to date have concentrated on the smaller cells for portable applications.

1.5 Battery Terminology

What we commonly call a battery is actually a cell. Strictly speaking a battery is a collection of individual cells, typically connected in series (i.e., car battery). In this thesis, the terms battery and cell will be used interchangeably. Discharge capacity, quoted in ampere-hours (A h), is equal to the amount of charge delivered during discharge. The average voltage at which the charge is delivered defines the amount of energy in the battery, where energy is the product of total capacity and average voltage (W h). Specific energy is the energy per unit mass (W h/kg). Energy density is the energy per unit volume (W h/L). Specific capacity describes the capacity per unit mass (mA h/g). Volumetric capacity describes the capacity per unit volume (mA h/cc). The terms anode and cathode refer to the direction of charge transfer at the interface between the electrode and the solution, strictly speaking, the terms should be interchanged during recharging. Potential confusion is avoided by simply referring to the electrodes as negative or positive. Cycling refers to repeated charge-discharge cycles. The host materials may be fully, or only partially, charged/discharged during cycling. Cycleability refers to the battery's ability to perform numerous cycles without appreciable loss of original capacity.

1.6 Scope of Research

The project includes the synthesis and characterization of new intercalation materials, and their processing into battery electrodes in the form of pellets, in order to develop accumulators exploiting lithium ion technology. The scope of this research is to synthesize various types of cathode materials from metal salts (as a metal source) and organic solvents (as a chelating agent). The synthesized cathode materials will be characterized by different analyses and instrumental techniques such as TGA-DTA (thermogravimetric-differential thermal analysis), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX), and Brunauer-Emmett and Teller (BET) surface area. The synthesized cathode materials used as the composite electrodes after cathode

fabrication. The synthesized cathodes were also characterized using various types of electro-analytical techniques and the results were compared with those of the parent cathode materials. The final step of the research is that the synthesized cathode electrodes were examined systematically in order to evaluate electrochemical performances of the lithium ion rechargeable battery. The focus of this work is on the development of a desirable cathode or positive electrode materials for lithium-ion batteries.

1.7 Research Objectives

Particularly the development of the active cathode materials preparation method is based on the trial and error approach guided by the background reading of the previous processes and reviewed articles. The following objectives have been addressed to testify the hypothesis:

1. To synthesize new mixture of metal oxides for the cathode portion of Li-ion battery
2. To make right combination of lithium with transition or nontransition metals by sol-gel method
3. To characterize the synthesized materials with numerous techniques in order to investigate the changes of physical and chemical properties
4. To increase the practical voltage around the theoretical voltage (6 volts)
5. To increase coulombic efficiency of Li-ion battery

1.8 Problems Statement and Solution Approach

The increased demand for power distribution systems, portable electronics and zero emission vehicles has led to the examination of the electrochemical battery as a solution to our energy storage needs. In particular, the rapid development in the

field of portable electronics including laptop computers, camcorders, cell phones and wireless communication devices require high energy density batteries to power them. Consumers have simple demands; they want a long lasting, lightweight, cheap, and safe battery. To meet these demands, the development of rechargeable (secondary) batteries has been the focus of considerable research. Portable, rechargeable lithium ion batteries offer several advantages when compared to current primary and secondary power sources. Lithium ion batteries have higher cell voltages 3.5-4.2 V (Plicht *et al.*, 1987; Megahed *et al.*, 1995; Berndt, 1997), higher energy density and longer cycle life. Improving the performance of current lithium-ion batteries in these three areas (voltage, energy density, and cycle life) is very important.

However, it is crucial to improve both the safety aspects of this high voltage system and the performance while using more abundant and low cost materials (Dai *et al.*, 2000). Many research groups have focused on improving the characteristics of the positive electrode, particularly developing high voltage cathode materials. Lithium manganese oxides spinel is an interesting and promising cathode material for rechargeable lithium batteries (Thackeray *et al.*, 1983; Tarascon *et al.*, 1991; Julien *et al.*, 1999). In comparison with layered LiCoO_2 and LiNiO_2 , its three-dimensional structure permits a reversible electrochemical extraction of Li^+ ions, at about 4 V versus Li/Li^+ , to $\lambda\text{-MnO}_2$ without lattice collapse (Thakeray *et al.*, 1984). Additional advantages are the relatively high theoretical capacity (148 mA h/g), low cost with ease preparation and environmental harmlessness (Tarascon *et al.*, 1994).

A problem to overcome for commercial application of this material is its fast capacity fading with charge/discharge cycling. This fact has been related to instability of the active phase caused by several possible factors like a slow dissolution of the cathode material into the electrolyte, high value of the relative volume changes accompanying charge/discharge cycling, Jahn-Teller distortion effect in deeply discharged electrodes (Rodriguez *et al.*, 1998; Gummow *et al.*, 1994). Presently, the capacity of lithium-ion batteries is limited by the capacity of cathode material. Though the commercially employed cathode, LiCoO_2 for Li-ion batteries

has a theoretical capacity of 274 mA h/g, the practical attainable capacity is found to be only 120-130 mA h/g in the voltage range 2.7-4.2 V (Fan *et al.*, 1998). The other viable and commercially available cathode material, lithium manganese oxide with the spinel structure LiMn_2O_4 , has a theoretical capacity of 148 mA h/g and its practically attainable value is 100-120 mA h/g (Aurbach *et al.*, 1999). In addition, LiMn_2O_4 is found to be unstable on cycling and shows severe capacity fading problems during cycling in the long run use. This can be overcome by doping various types of metals such as Cr, Zn, Fe, Al, Ni, Ga, Mg, V, Cu in LiMn_2O_4 . The addition of dopants, may also decrease the initial capacity of the cell.

Amine *et al.*, 1997 found a way to engineer a 5 volt battery to have consistently high capacity for multiple cycles. They prepared $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_4$ using sol-gel method and was the first made and tested in mid 1990s. The material has been shown to have a high voltage reaction at 4.7 V. Doping of the transition metals such as Ni, Fe, Co, Cr etc in lithium rich spinels considerably improved the rechargeability on cycling but they delivered significant loss of the initial capacity. An improved operational capacity may be achieved by using LiNiO_2 and its derivatives (Fan *et al.*, 1998; Chowdari *et al.*, 2001). The latter materials, however, are not stable on cycling and their cathodic capacity fades drastically, especially when charged and discharged at high current rates. The unsafe operation of these materials is also of concern. Therefore, to realize cost effective Li-ion batteries, the challenge is to identify an alternate cathode material with higher capacity which is cheaper, safe and non-toxic to replace LiCoO_2 (Shaju *et al.*, 2002).

The stoichiometry, crystal structure and morphology of the active materials are of essential importance for its electrochemical properties (Gadjov *et al.*, 2004). All these factors are closely related to the method of synthesis. Many procedures for the preparation of cathode materials have been proposed in the literature during last years. The classical ceramic synthesis by a solid-state-reaction between oxides (Guan *et al.*, 1998; Yamada *et al.*, 2000) has been used extensively, but it requires prolonged heat treatment at relatively high temperatures (>700 °C) with repeatedly intermediate grinding. Moreover, this method does not provide good control on the

crystalline growth, compositional homogeneity, morphology and microstructure. As a consequence, the final product consist in relatively large particles ($>1 \mu\text{m}$) with broad particle size distribution.

In order to overcome these disadvantages, various preparative techniques, known as “soft-chemistry” methods, have been developed. Such techniques are based on the processes of co-precipitation, ion-exchange or thermal decomposition at low temperature of appropriate organic precursors obtained by sol-gel synthesis (Hernan *et al.*, 1997; Kang *et al.*, 2000), Xero-gel (Prabaharan *et al.*, 1995), Pechini (Liu *et al.*, 1996; Liu and Kowal *et al.*, 1996), freeze-drying (Zhecheva *et al.*, 1999), and emulsion-drying (Hwang *et al.*, 1998) methods. This soft chemistry techniques offer many advantages (Thirunakaran *et al.*, 2004) such as better homogeneity, low calcination temperature, shorter heating time, regular morphology, sub-micron sized particles, less impurities, large surface area, and good control of stoichiometry.

In the last 20 years, the lithium-ion battery has become a highly researched topic. The high voltage and energy capacity of the system classify the lithium-ion battery as the most promising energy storage source. However, several improvements must be made before the battery is recognized as a dependable power source for all high voltage applications.

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