



**Interlayer Mixing in Lithium Nickel Manganese  
Cobalt Oxide Cathode Materials for Rechargeable  
Lithium Batteries**

by

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## DECLARATION OF THESIS

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## LIST OF ABBREVIATIONS

Co	Cobalt
DMC	Dimethyl carbonate
EC	Ethylene carbonate
EVs	Electric vehicles
GSAS	General Structure Analysis System
Li	Lithium
Li[PF <sub>3</sub> (C <sub>2</sub> F <sub>5</sub> ) <sub>3</sub> ]	Fluoroalkylphosphates
Li <sub>15</sub> Si <sub>4</sub>	Lithium silicides
Li <sub>2</sub> MnO <sub>3</sub>	Lithium manganese oxide
LiCoO <sub>2</sub>	Lithium cobalt oxide
LiFePO <sub>4</sub>	Lithium iron phosphate
LiNiO <sub>2</sub>	Lithium nickel oxide
LiPF <sub>6</sub>	Lithium hexafluorophosphate
Mn	Manganese
Ni	Nickel
Ni-Cd	Nickel cadmium
Ni-MH	Nickel-metal hydride
NMP	N-methylpyrrolidone
O <sub>2</sub>	Oxygen
PVDF	Polyvinylidene difluoride binder
TGA	Thermogravimetric analysis
XRD	X-ray Diffraction

## LIST OF SYMBOLS

$2\theta$	Diffraction angle
$\lambda$	wavelength
$\chi^2$	Reduced Chi <sup>2</sup>

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3.3	Lorentzian component: $\text{FWHM} = (X \tan \theta + Y / \cos \theta)^{1/2}$	45
3.4	$\chi^2 = \left( \frac{R_{wp}}{R_{exp}} \right)^2$	46

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## Pencampuran antara Lapisan dalam Bahan Katod Litium Nikel Mangan Kobalt Oksida untuk Bateri Litium Cas Semula

### ABSTRAK

Komposisi  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  dan analoginya  $\text{Li}[(\text{Ni}_{0.5}\text{Mn}_{0.5})_{1-x}\text{Co}_x]\text{O}_2$  telah disintesis menggunakan kaedah tindak balas keadaan pepejal konvensional untuk menilai kesan pengurangan kandungan kobalt dalam bahan katod bateri yang berstruktur garam batu berlapis. Analisis struktur menggunakan kaedah penyaringan Rietveld menggunakan data XRD konvensional telah mendedahkan bahawa kandungan kobalt adalah saling berhubungkait dengan kestabilan struktur bahannya. Had larutan pepejal bagi sampel fasa-tulen yang disintesis ialah sekitar  $x \geq 0.2$  untuk  $\text{Li}[(\text{Ni}_{0.5}\text{Mn}_{0.5})_{1-x}\text{Co}_x]\text{O}_2$ . Jumlah pencampuran antara lapisan telah meningkat bagi sampel yang mengandungi 20% atau kurang kandungan kobalt. Keputusan menunjukkan jumlah pencampuran antara lapisan paling minima yang boleh dicapai ialah lebih kurang 3.8% bagi komposisi  $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$  yang disintesis pada suhu  $950^\circ\text{C}$  dalam oksigen berbanding dengan  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  iaitu sekitar 2%. Walau bagaimanapun, jumlah pencampuran antara lapisan berbeza-beza mengikut perubahan suhu dan keadaan sintesis. Kajian sistematik telah dijalankan untuk mengoptimumkan parameter penyaringan dan mengesahkan model struktur berdasarkan  $\text{LiCoO}_2$  sebagai piawaian. Di samping itu, kapasiti cas dan discas permulaan semasa kitaran bateri untuk  $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$  adalah agak tinggi dengan mencatat masing-masing ialah  $\sim 323 \text{ mAh g}^{-1}$  dan  $\sim 229 \text{ mAh g}^{-1}$ . Namun begitu, ia mempunyai kehilangan kapasiti tidak boleh diubah yang tinggi selepas beberapa kitaran yang mungkin disebabkan oleh ketidakstabilan struktur semasa cas dan discas.

## Interlayer Mixing in Lithium Nickel Manganese Cobalt Oxide Cathode Materials for Rechargeable Lithium Batteries

### ABSTRACT

Composition of  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  and its analogous  $\text{Li}[(\text{Ni}_{0.5}\text{Mn}_{0.5})_{1-x}\text{Co}_x]\text{O}_2$  were prepared by conventional solid state method to evaluate the effect of reducing cobalt contents to the layered rock salt-type cathode materials. Structural analysis using Rietveld refinement of conventional XRD data revealed that the amount of cobalt contents is highly correlated to their structural stability. Solid solution limit for phase-pure samples that were prepared is about  $x \geq 0.2$  for  $\text{Li}[(\text{Ni}_{0.5}\text{Mn}_{0.5})_{1-x}\text{Co}_x]\text{O}_2$ . The amount of interlayer mixing increased for samples contain 20% or less cobalt contents. The results showed that the minimum amount of interlayer mixing that could be achieved is about 3.8% for the composition of  $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$  that was prepared at 950 °C in oxygen compared to  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  which is about 2%. However, the amount of interlayer mixing varies as a function of temperatures and conditions. Systematic investigation have been done to optimize refinement parameters and to validate structural model based on  $\text{LiCoO}_2$  as a standard. On the other hand, the initial charge and discharge capacities during battery cycling for  $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$  is relatively high which recorded  $\sim 323 \text{ mAh g}^{-1}$  and  $\sim 229 \text{ mAh g}^{-1}$  respectively. But it has high irreversible capacity loss after a few cycles that are probably due to structural instability during charge and discharge.

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# CHAPTER 1

## INTRODUCTION

### 1.1 Background

Nowadays, batteries are the main source of power for portable electronic devices and also for automobile starting and ignition. The increasing global energy demands and the arising of environmental concerns have caused batteries to be intensively pursued for a widespread hybrid electric vehicle (HEV) and plug-in hybrid electric vehicle (PHEV) applications. The batteries performances are affected by the materials used and the engineering involved in fabricating them (Arumugam, 2010).

Batteries are commonly classified into primary and secondary batteries. Primary batteries cannot be electrically charged because there are irreversible chemical reactions involved in the electrode materials (Arumugam, 2010). However, they provide good storage characteristics and high energy density. They existed in many forms, for instances, lithium-thionyl chloride, lithium-carbon monofluoride and lithium-manganese dioxide batteries. These batteries have been commercialised for more than 30 years. Other batteries such as carbon-zinc, alkaline-manganese, zinc-air, and silver oxide-zinc batteries are used together with these batteries.

Secondary batteries which are opposed to primary batteries can be electrically charged, and these batteries can save costs and resources. For example, lithium-ion and nickel-metal hydride batteries have been produced, and are used with the other secondary batteries, such as lead-acid, nickel-cadmium and coin-type lithium secondary batteries. The diversity and the applications for conventional and new practical battery systems have been increasing for the last 30 years.

### **1.1.1 Lithium ion batteries**

Lithium-ion batteries which are in the family of rechargeable batteries are also well known as the most important energy storage device. They are lighter, can last for longer time and quicker to charge compared to their nickel-based relatives. The worldwide market for rechargeable lithium-ion batteries are now valued at 10 billion dollars per annum and is arising. Such rapid growth is mainly due to its higher energy density and better cycling performance than other energy storage devices. Recent demands on energy and environmental sustainability have further urged significant interest in a larger scale lithium-ion battery system for vehicles and grid load leveling (Choi, Wang, & Yang, 2011).

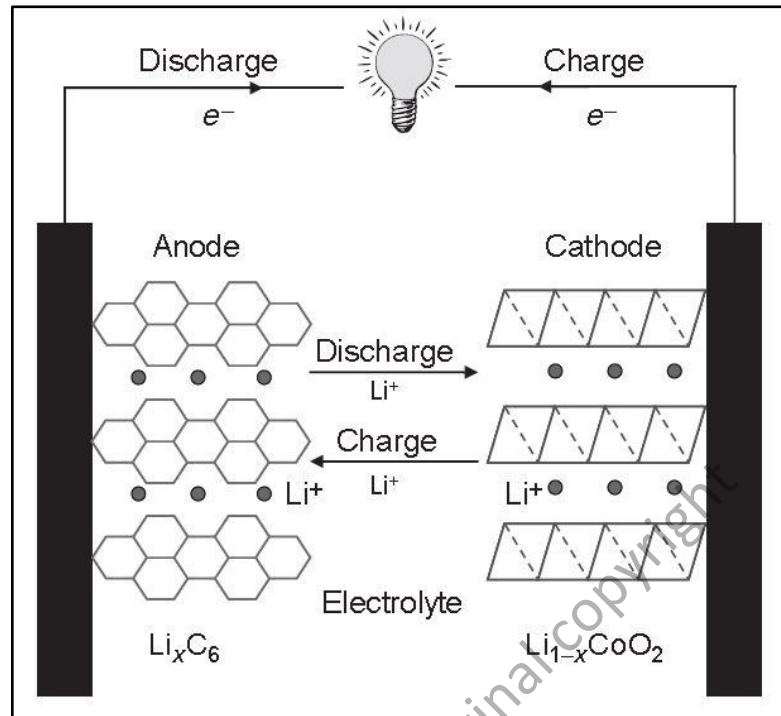
The lithium-ion batteries have a quite straightforward energy storage mechanism in which they store electrical energy in electrodes that are made of lithium-intercalation (or insertion) compounds with reduction and oxidation processes occurring simultaneously at the two electrodes (Choi, Wang, & Yang, 2011). Lithium-ion batteries usually consist of complex lithium oxides containing a transition metal oxide as the positive electrode (cathode) material, a carbon material as the negative electrode

(anode) material and organic solvent as electrolyte between these two electrodes (Nishio & Furukawa, 1999).

The lithium ion secondary battery (LIB) technology was initiated by Sony Corporation which brought out the lithium ion cells into the market first in the world in 1991. Some basic characteristics of LIB are as follows (Yoshio, 2000).

- a. high energy density (both gravimetric and volumetric),
- b. high operating voltage,
- c. no memory effect,
- d. high drain capability,
- e. quick charge acceptance,
- f. low self-discharge rate,
- g. wide temperature range of operation

When the cell is fabricated, it is in the discharge condition. When it is charged, both lithium ions and electrons move from the positive electrode to the negative electrode. The lithium ions move through the electrolyte whereas the electrons move through the external circuit during charging. Generally, the cells voltage will become higher as the potential of the cathode rises and that of anode is lowered during charging. When a load is connected between the positive and negative electrodes, the cell is discharged where the lithium ions and electrons move from the negative electrode to the positive electrode. Electrical energy is obtained as a result of the diffusion of lithium ions and electrons (Nishio & Furukawa, 1999). Fig. 1.1 illustrated the movements of lithium ions and electrons during charging and discharging. (Arumugam, 2010).



**Figure 1.1:** Diagram of the movements of lithium ions and electrons during charging and discharging (Arumugam, 2010).

### 1.1.2 Components of lithium ion batteries

As mention before, there are three main components in lithium ion batteries which include negative electrode (anode), electrolyte and positive electrode (cathode).

#### i. Negative electrode (anode)

In lithium ion battery, the anode is the negative electrode of a cell where oxidative chemical reactions occurred. During discharge, it releases electrons into the external circuit (Whittingham, 2004). There are a wide range of materials with potential and practical applications in the field of anode materials for lithium-ion batteries.

Initially, Li metals which have high energy density are used as anode. Since Li metals are very active, a passivating surface layer is formed on the lithium anode when Li reacts with the electrolyte. This protection layer prevents further reaction because it is an electronic insulator and a lithium ion conductor (Wakihara & Yamamoto, 1998). The usage of Li metal and alloys as the anode materials were until the 1980s due to safety issue (Aifantis & Hackney, 2010). However, lithium alloy anode materials have been reviewed focusing on the lithium alloying in Group IV and V elements and their composites from mechanistic aspects of (Park *et al.*, 2010).

In the past, carbon that is low cost, easily available and possible to be modified made it hard to be replaced by other anode material. Many researchers have been studied in depth on the alternative forms of carbon materials and their corresponding reaction mechanism, surface effects, new nano-materials and so on (Alcántara *et al.*, 2011). After year 1991 in which Sony Energytec Inc. first commercialised the lithium ion battery, graphite has become the standard anode for lithium ion batteries. It has a specific capacity of 300 mAh g<sup>-1</sup> (Kendrick & Slater, 2011) However, the theoretical capacity (372 mAh g<sup>-1</sup>) is poor compared with the charge density of lithium (3,862 mAh g<sup>-1</sup>). Hence, novel graphite varieties and carbon nanotubes have been proposed to improve the capacity but they encountered with high processing costs (Wakihara & Yamamoto, 1998).

Apart from carbonaceous material, there are a few materials which have drawn interests of many researchers. These include transition metal oxides, nitrides, phosphides, antimonides, silicon and silicon compound, last but not least, tin and tin alloy compounds.