SYNTHESIS AND CHARACTERISATION OF TERNARY SYSTEM $LiCoPO_4$–$LiNiPO_4$–$LiMnPO_4$ CATHODE MATERIALS FOR Li-ION BATTERIES

by

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LIST OF ABBREVIATIONS

CPE	Constant Phase Element
DEC	Diethyl Carbonate
DMC	Dimethyl Carbonate
EIS	Electrochemical Impedance Spectroscopy
EC	Ethylene Carbonate
FWHM	Full Width Half Maximum
GSAS	General Structure Analysis System
HEV	Hybrid Electric Vehicles
ICSD	Inorganic Crystal Structure Database
ICDD	International Center for Diffraction Data
JCPDS	Joint Committee for Powder Diffraction Studies
LIB	Lithium-ion batteries
PVDF	Poly (Vinylidene fluoride)
PDF	Powder Diffraction File
PC	Propylene Carbonate
SEM	Scanning electron microscopy
VESTA	Visualization for Electronic and Structural Analysis
XRD	X-ray diffraction

LIST OF SYMBOLS

E_a	Activation energy
Y	Admittance
ω	Angular frequency
k	Boltzmann's Constant
Q	Charge
R_{ct}	Charge transfer resistance
L	Crystallite size
°C	Degree celsius
θ	Diffraction angle
σ	Electrical conductivity
β	Full Width Half Maximum
h	Hours
Z″	Imaginary part of Impedance
d	Interplanar spacing
ε	Lattice strain
Z′	Real part of Impedance
S	Siemens
V	Voltage
λ	Wavelength of X-rays

LIST OF EQUATIONS

Sintesis dan Pencirian Bahan Katod dalam Fasa Segitiga $LiCoPO_4$–$LiNiPO_4$–$LiMnPO_4$ untuk Bateri Lithium Ion

ABSTRAK

Peranti penyimpanan tenaga elektrokimia dengan ketumpatan tenaga yang tinggi adalah penting dalam masyarakat moden. Bahan katod yang mempunyai voltan nyahcas dan kapasiti nyahcas yang tinggi diperlukan untuk mendapatkan bateri litium yang mempunyai ketumpatan tenaga yang tinggi. Oleh itu, bahan katod voltan tinggi seperti olivine Li*M*PO_4 (*M* = Mn, Co, and Ni) dan spinel $Li_2CoMn_3O_8$ telah dikaji secara meluas oleh penyelidik-penyelidik. Dalam kajian ini, tiga siri analog dengan formula $LiCo_{1-x}[Ni_{0.5}Mn_{0.5}]_xPO_4$, $LiNi_{1-x}[Co_{0.5}Mn_{0.5}]_xPO_4$ dan $LiMn_{1-x}[Co_{0.5}Ni_{0.5}]_xPO_4$ ($0 \leq x \leq 1$) yang berstruktur olivine dalam fasa segitiga $LiCoPO_4$ – $LiNiPO_4$ – $LiMnPO_4$ telah dikaji secara sistematik sebagai calon berpotensi untuk bateri litium cas semula yang beroperasi pada voltan tinggi. Sampel-sampel telah disediakan melalui kaedah sintesis keadaan pepejal konvensional. Semua sampel telah dipanaskan pada suhu 750–1000 °C dalam udara selama 12 jam dengan dua pendekatan pendinginan yang berbeza, iaitu pendinginan perlahan dan pelindapkejutan. Pencirian komposisi-komposisi ini telah dilakukan dengan menggunakan Pembelauan sinar-X (XRD), Mikroskop Imbasan Elektron (SEM) dan Analisis Impedans Spektroskopi. Pada mulanya, $LiCoPO_4$, $LiNiPO_4$ dan $LiMnPO_4$ telah disintesis dan telah digunakan sebagai rujukan piawaian. Analisis XRD menunjukkan bahawa semua sampel yang disintesis telah mencapai fasa tulen dan kestabilan struktur sehingga suhu 1000 °C. Semua sampel mempunyai struktur olivine dengan kumpulan ruang *Pnma*. Analisis struktur yang menggunakan kaedah penyaringan Rietveld menggunakan data XRD konvensional telah mendedahkan bahawa anggaran jumlah kecacatan kekisi (*anti-site*) adalah rendah iaitu kurang daripada ~ 5%. Perubahan parameter kekisi bagi sampel ketiga-tiga siri adalah selaras dengan hukum Vegard. Perbandingan struktur dan sifat elektrik antara sampel yang dilindapkejut dengan sampel yang didinginkan dengan perlahan telah dilakukan. Keputusan menunjukkan bahawa jumlah kecacatan kekisi (*anti-site*) dalam kedua-dua kaedah pendinginan mempunyai nilai yang lebih kurang sama. Walau bagaimanapun, semua sampel menunjukkan sifat keberaliran elektrik hakiki yang rendah iaitu sekitar 10^{-8} S cm^{-1} apabila diukur dengan LCR meter pada suhu 300 °C. Oleh itu, kajian lanjut telah dilakukan pada $LiNi_{1/3}Mn_{1/3}Co_{1/3}PO_4$ untuk meningkatkan kekonduksiannya. $LiNi_{1/3}Mn_{1/3}Co_{1/3}PO_4$ telah diproses dengan menggunakan kaedah pengisaran bebola untuk mengurangkan saiz zarah. Selepas itu, $LiNi_{1/3}Mn_{1/3}Co_{1/3}PO_4$ telah dicampur dengan pelbagai bahan bersumber karbon: graphene nano-platelets (GNP), nanotiub karbon (CNT) and hitam karbon (CB) untuk membentuk komposit. Keputusan menunjukkan bahawa komposit-komposit $LiNi_{1/3}Mn_{1/3}Co_{1/3}PO_4$/C mempunyai kekonduksian yang lebih tinggi berbanding dengan $LiNi_{1/3}Mn_{1/3}Co_{1/3}PO_4$ yang tanpa pengubahsuaian. Oleh itu, pengubahsuaian melalui pemprosesan tersebut berkemungkinan boleh digunakan untuk meningkatkan kekondukisian ketiga-tiga siri analog tersebut. Selain itu, satu lagi penyelidikan sampingan turut dijalankan untuk mengkaji kesan penggantian Zn dalam $Li_2CoMn_3O_8$, walau bagaimanapun, hasilnya tidak begitu memuaskan kerana sampel yang mengandungi Zn menunjukkan kapasiti nyahcas yang rendah.

Synthesis and Characterisation of Ternary System $LiCoPO_4$–$LiNiPO_4$ – $LiMnPO_4$ Cathode Materials for Li-ion Batteries

ABSTRACT

Electrochemical energy storage devices with high energy density are important in modern society. In order to obtain high energy density Li ion batteries, cathode materials with high discharge voltage and discharge capacity are required. Hence, high voltage cathode materials such as olivine Li*M*PO_4 (*M* = Mn, Co, and Ni) and spinel $Li_2CoMn_3O_8$ have been extensively studied by researchers. In this study, three analogous series with the formula of $LiCo_{1-x}[Ni_{0.5}Mn_{0.5}]_xPO_4$, $LiNi_{1-x}[Co_{0.5}Mn_{0.5}]_xPO_4$ and $LiMn_{1-x}[Co_{0.5}Ni_{0.5}]_xPO_4$ ($0 \leq x \leq 1$) within the phase triangle of $LiCoPO_4$ – $LiNiPO_4$ – $LiMnPO_4$ were systematically studied as potential candidates for high voltage rechargeable lithium ion batteries. The samples were synthesized by conventional solid state route at temperature 750–1000 °C in air for 12 hours with two different cooling conditions (i.e. slow cooling and quenching). These compositions were characterised by using X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Impedance Spectroscopy Analyser. Initially, $LiCoPO_4$, $LiNiPO_4$ and $LiMnPO_4$ were prepared as end members and were used as standard references. The prepared samples were single phase and structurally stable up to 1000 °C. All the XRD patterns could be indexed with the olivine structure and the space group of *Pnma*. Structural analysis using Rietveld refinement of conventional XRD data revealed that the estimated anti-site defects was comparably low which is less than ~5 %. The changes in lattice parameters across the series Mn, Co and Ni were in accordance with Vegard's law. The structure and electrical properties of the slow-cooled and quenched samples were compared. The results showed that the anti-site defects in both the quench and slow-cooled samples have quite similar values. Nevertheless, all the samples exhibits low intrinsic electrical conductivities of about ~10^{-8} S cm^{-1} that were measured using a LCR meter at 300 °C. Hence, further modification were performed on complex olivine $LiNi_{1/3}Mn_{1/3}Co_{1/3}PO_4$ in order to improve the conductivity. $LiNi_{1/3}Mn_{1/3}Co_{1/3}PO_4$ was ball milled to reduce the particle size followed by ball milling with three different carbon sources: graphene nano-platelets (GNP), carbon nanotube (CNT) and carbon black (CB) to form composites. The results showed that these composites have exhibited relatively higher coin cell conductivity compare to the bare sample. Hence, it was believed that this processing route can probably be applied to improve the conductivity of the three analogous series. On the other hand, a small research was also carried out to study the effect of Zn doped into spinel $Li_2CoMn_3O_8$, however, the result was not quite promising because the doped samples exhibited low discharge capacity.

CHAPTER 1 : INTRODUCTION

1.1 Background

The research of lithium battery began in the 1950s, while research and development of the rechargeable Li-ion batteries (LIBs) began in the early 1980s at Asahi Chemicals (Brodd, 2009). LIBs have become a commercial reality in 1991 when the engineers from Sony managed to surprise the "battery world" by commercializing Li-ion battery (LIBs) which is based on a lithiated carbon anode and $LiCoO_2$ as cathode. Since then, LIBs have been one of the most promising chemical-electrical energy conversion power sources owing to their outstanding properties which include higher energy density and operating voltage as compared to nickel metal hydride (Ni-MH) and lead acid batteries (Broussely, Biensan, & Simon, 1999). Diouf & Pode (2015) have disclosed the variety potential of the use of LIBs as primary energy storage substituting the very common lead acid batteries.

Figure 1.1 shows that LIBs are most suitable for consumer electronic devices because they are lighter and smaller than other rechargeable batteries for the same energy storage capacity. Nowadays, it is believed that the driving force for the development of LIBs in renewable energy sector could be the electric vehicle and the smart grid industry. Hence, improving the energy density of batteries is utmost urgent. Huggins (2009) introduced the concept of energy quality which can be defined as the amount of useful power or product that a unit energy can provide. In response to this concept, high voltage energy is similar to high temperature heat whereby it is often more useful as demonstrated in Figure 1.2a owing to the square relationship between the electrical power (P) and the

practical voltage (V) ($P = V^2/R$). Hence, an ideal LIB must fulfil the requirement of high capacity and high operating voltage. In other words, both electrodes need to have high specific capacity besides having high discharge voltage for cathode materials and low charge voltage for anode materials (Fig. 1.2b). However, in reality, cathode materials usually have to compromise between the discharge voltage and the specific capacity. For example, it can be observed from Figure 1.2c, $LiNi_{0.5}Mn_{1.5}O_4$ can achieve specific capacity of about 120 mAh g^{-1} when the discharge voltage is high (~4.8 V) but $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ can exhibit specific capacity above 200 mAh g^{-1} with intermediate discharge voltage of about 3.6 V. Nonetheless, there are many more issues to be concerned before the commercialization of LIB using these electrodes. The development of energy storage is a continuing challenge for researchers to pursue higher performance and to sustain the environment for future generations as well.

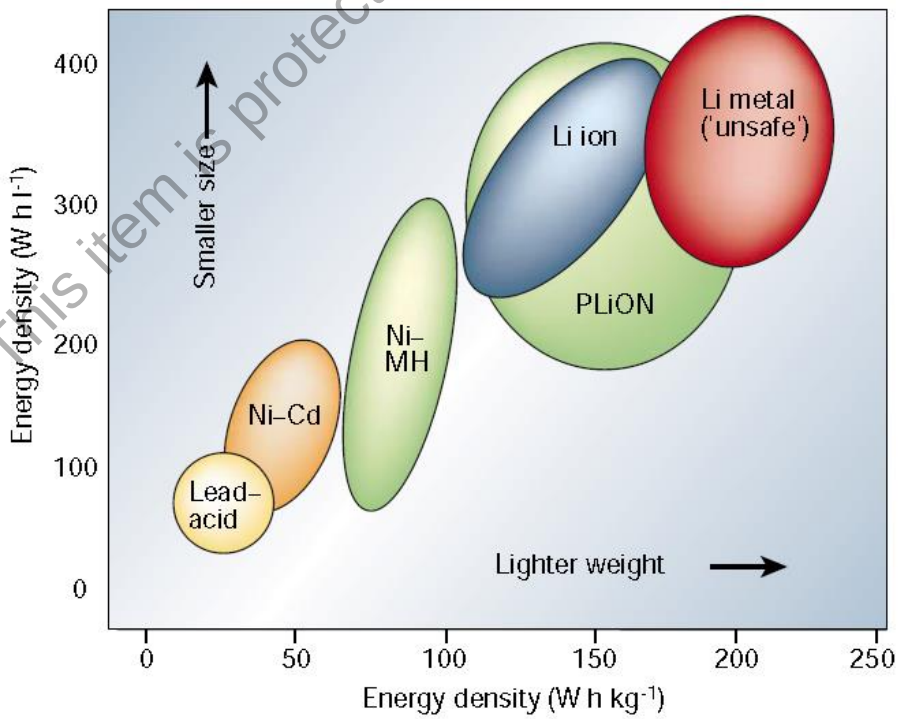

Figure 1.1: Comparison between different battery technologies in term of volumetric and gravimetric energy densitites (Tarascon & Armand, 2001).

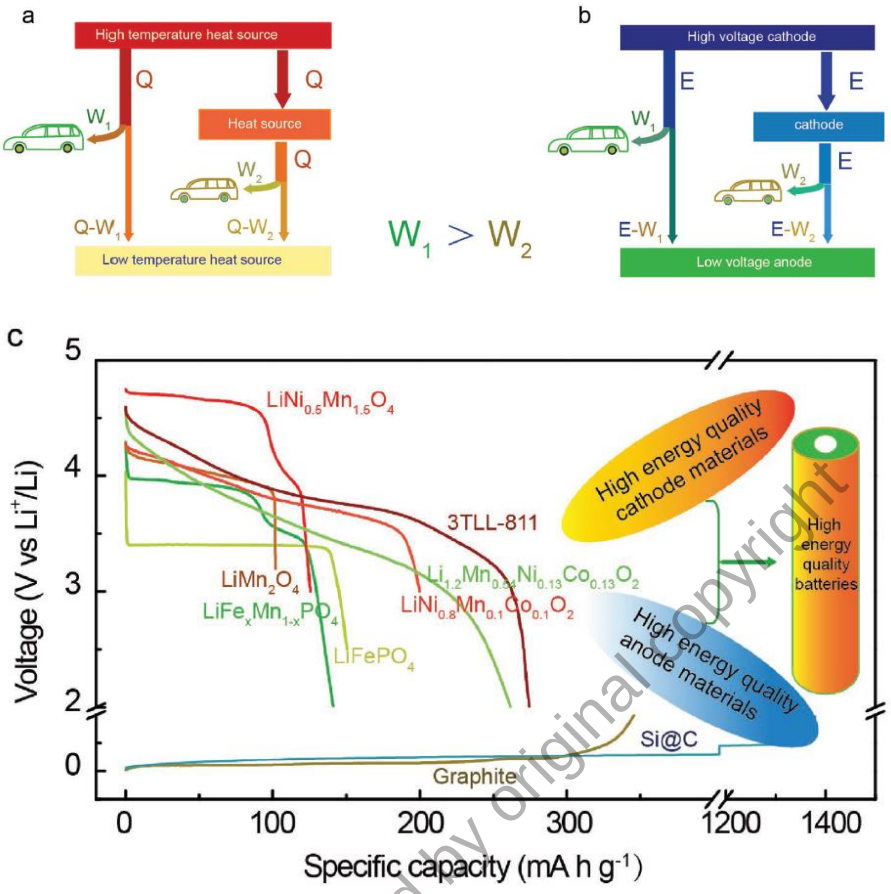

Figure 1.2: Schematic of (a) heat quality (b) energy quality, showing analogous to the concept of heat quality, in which high voltage energy similar to high-temperature heat can be more useful. (c) Comparison between several high energy quality of cathodes and anodes (Shi *et al.*, 2018).

1.1.1 Basic Operating Principle of Li-ion Batteries

In the most basic sense, a standard Li-ion battery usually refers to a battery which consists of cathode (positive electrode) and anode (negative electrode) materials serve as a host for the Li ions (Li^+). The anode and cathode are separated by an ionically conductive but electronically insulating electrolyte, separator and current collector (mostly Al and Cu) as depicted in Figure 1.3 (Rommel, Schall, Brünig, & Weihrich, 2014). The common concept of present LIBs relies on transition metals oxides or phosphates ($LiCoO_2$, $LiMn_2O_4$, $LiCo_{1/3}Mn_{1/3}Ni_{1/3}O_2$, $LiFePO_4$, etc.) as cathode active material, while graphite is commonly used as anode active material. A separator in