PREPARATION AND CHARACTERIZATION OF BINARY AND TERNARY TIN-BASED ALLOY POWDERS FOR LITHIUM ION BATTERY

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To my family who offered me unconditional love and support throughout the course of this report

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In the name of Allah, The Most Merciful and Most Compassionate

Indeed all praise is for Allah, we praise Him, we ask for His help, and for his forgiveness. We seek Allah's refuge from the evils of ourselves and from our evil actions. Whomever Allah guides, then none can lead him astray, and whomever Allah misguides, then none can guide him. I testify that none has the right to be worshipped, except Allah, alone, having no partner, and I testify that Muhammad is His Slave and His Messenger.

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ABSTRACT

Binary and ternary Sn-based alloy powders were successfully prepared by chemical reduction method. The physical properties of the alloy powders were determined by X-ray diffraction, field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDX), and nitrogen adsorption method. From the X-ray diffractogram showed that introduction of high concentration of third elements (Mn and Fe) caused the peaks to become more distinct as compared to the binary alloys. Increasing stirring time decreased the crystallite size as calculated using Scherrer's equation. Analysis by using FESEM showed that high composition of third element in Sn-Co system gave spheroid particles in the range of 36.4 to 73.5 nm. Elemental analysis of ternary Sn-based alloy powders synthesized by chemical reduction method was studied using EDX showed the existence of each elements used in the binary and ternary alloy powders. Binary and ternary Sn-based alloy powders showed similar trends for all cycles in charge/discharge test. The first cycle exhibits higher discharge capacity compared to the second and third cycles. Large difference between the experimental and the theoretical values in alloy powders may be due to the formation of solid electrolyte interphase, irreversible Li trapping during charging process and disintegration of the electrode.

ABSTRAK

Serbuk aloi binari dan ternari berasaskan stanum telah berjaya dihasilkan menggunakan kaedah penurunan kimia. Sifat fizik serbuk aloi ditentukan dengan pembelauan sinar-X (XRD), mikroskopi imbasan electron pancaran medan (FESEM), spektroskopi sinar-X serakan tenaga (EDX) dan kaedah penjerapan nitrogen. Difraktogram sinar-X menunjukkan penambahan komposisi yang tinggi unsur ketiga menjadikan puncak yang terhasil lebih jelas berbanding aloi binari. Peningkatan masa pengacauan menyebabkan saiz zarah semakin mengecil berasaskan pengiraan menggunakan persamaan Scherrer. Analisis FESEM menunjukkan kepekatan unsur ketiga yang tinggi dalam sistem Sn-Co memberikan saiz zarah berbentuk sfera dalam julat 36.4 - 73.5 nm. Analisis unsur pada serbuk aloi ternari berasaskan stanum yang disintesis menggunakan penurunan kimia telah dikaji menggunakan EDX. Serbuk aloi binari dan ternari berasaskan stanum menunjukkan tren yang sama bagi semua kitaran semasa ujian cas dan nyahcas. Kitaran pertama mempamerkan kapasiti nyahcas yang lebih tinggi berbanding kitaran kedua dan ketiga. Perbezaan yang besar antara data eksperimen berbanding teori mungkin disebabkan pembentukan interfasa pepejal elektrolit, pemerangkap Li tidak berbalik semasa proses cas dan perpecahan elektrod.

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LIST OF ABBREVIATIONS AND SYMBOLS

AAO	-	Anodic alumina oxide
CNF	-	Carbon nanofiber
CVD	-	Chemical vapor deposition
D	-	Crystallite size
Ď	-	Chemical diffusion coefficient
DMC	-	Dimethyl carbonate
EC	-	Ethylene carbonate
HEMM	-	High-energy mechanical milling
KS6	-	Type of synthetic graphite
LIBs	-	Lithium ion batteries
MA	-	Mechanical alloying
mA	-	Miliampere
mAh/g	-	Capacity unit (miliampere hour per gram)
MCMB	-	Mesocarbon microbeads
MWNT	-	Multi-walled carbon nanotube
rf	-	Radio frequency
SEI	-	Solid electrolyte interphase
SWNT	-	Single-walled carbon nanotube
TEM	-	Transmission electron microscopy
X	-	Elements used (Cu, Mn, Fe)
Z	-	Atomic number

CHAPTER 1

INTRODUCTION

1.1 Research Background

Alternative energy conversion and storage system have gained more attention as the present energy based is at serious risk. Current energy based on fossil fuel faced depletion due to continuous demand of oil (Lin *et al*., 2010; Scrosati and Garche, 2010). Besides, the environmental concerns also encouraged the replacement of fossil fuel energy based. Thus, many studies have been carried out with a view to find high efficiency energy storage system. As an alternative energy sources, lithium ion battery shows high energy density.

Commercialized rechargeable lithium ion battery has carbon and cathode metal oxide ($LiCoO_2$) (Huang *et al*., 2009). Based on the graphite anode, cathode metal oxide and electrolyte, this new energy sources have been widely used in portable electronic devices (laptop, hand phone, camera) and electric vehicles. Energy formed by this new system defeated conventional lead acid and nickel cadmium batteries. Lithium ion batteries have high energy density as it provides 1.5 times much energy than conventional battery (Wakihara, 2001).

Increasing demand for higher capacity batteries had driven the researchers to improve more from the current existed lithium ion batteries. Generally, the most common anode being used are graphite and hard carbon based (Li *et al*., 1999). In the lithium ion batteries system, graphite will react with lithium to form LiC_6 and deliver

372 mAh/g (Hirai *et al.*, 2006). Due to that problem, other materials need to be discovered to replace the low performance of graphite anode. Large numbers of experimental approaches have been proposed to increase the anode's electrochemical capacity and performance. Among all those, tin (Sn) become the most attractive material due to its high specific capacity compare to graphite.

Hang *et al*., (2007) reported that improvement of battery should fulfill some criteria. The improved battery should operate safely at higher current density and low temperature. It should also have higher specific capacity compare to current electrode capacity and better cycling behavior. Besides that, a good battery must give less irreversible capacity in the first cycle and low production cost. The replacement of graphite material to Sn material in anode will hopefully achieve the criteria of good battery and hence improve the performance of lithium ion batteries. Therefore, Sn is a very promising material in lithium ion battery. In previous study, introduction Sn based as an anode showed positive result. It showed significant advantages over graphite including high reversible capacity and also lower irreversible capacity (Wan *et al*., 1998).

In recent years, many efforts have been made for preparing Sn based anode via different approaches. These method includes mechanical ball milling (Li *et al*., 1999), electron beam deposition (Hu *et al*., 2009), hydrothermal (Kumar *et al*., 2004), macro-encapsulation (Wang *et al.*, 2004), radio frequency (rf)- magnetron sputtering (Seung *et al*., 2002) and chemical reduction (Wu *et al*., 2009). Among all these method, chemical reduction showed some advantages including simple operation, low cost and fast reaction. By using mechanical ball milling, particles are easily aggregate and become larger. It also consumes high energy and cost. Hydrothermal reaction is not suitable method due to high temperature condition while micro-encapsulation took longer period to complete reaction. High power consuming when the used of radio frequency (rf)- magnetron sputtering also limit this application method. Based on the previous method used, chemical reduction has been selected not just because of its simplicity but also able to produce good morphology and give excellent electrochemical performance (Wang *et al*., 2007).

1.2 Problem Statement

Tin (Sn) is one of the most attractive materials in anode for lithium ion batteries due to its large capacity compared to current graphite anode. It is also has high packing density and thermodynamic potential (Guo *et al*., 2007). However, the application of Sn as the anode has been hindered by the rapid capacity fading upon cycling due to drastic volume changes (Yang *et al.*, 2001). The problem of large volume expansion and interaction in Li^+ insertion/extraction will reduce the mechanical stress within materials, leading to electrode pulverization and loss cyclability in application. Severe degradation of the anode upon cycling and shortens the life cycle of electrode will occur due to mechanical loss of active materials (Huang *et al*., 2009). In order to overcome this problem, the need to pair pure Sn with better properties active materials which could possibly give a lower capacity fading is a necessary task. A challenge in development of lithium ion batteries is to fulfill the criteria of low cost of production good lithium ion batteries in terms of its quality, surface morphology, cycle stability and high energy density. Combination of pure Sn with other material was known to give strengthen to the electrode. Thus, several transition metals have been selected to be pair with Sn since those transition metals have the characteristics of high mechanical strength and electric conductivity.

1.3 Objectives

The objectives of this research are:

i) To prepare ternary Sn-based alloy powders.

ii) To characterize the physical properties of ternary Sn-based alloy powders.

iii) To characterize the electrochemical performance of ternary Sn-based alloy powders.

1.4 Scope of the Study

Scope of this study consists of 3 parts:

i) Preparation of Sn-based alloy powders as anode
   a) Preparation of Sn-Co alloy powders as the reference for ternary Sn-based alloy powders.
   b) Preparation of Sn-Co-Cu, Sn-Co-Mn, Sn-Co-Fe alloy powders by chemical reduction process with various concentration and stirring time.

ii) Characterization of physical properties of ternary Sn-based alloy powders by using X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-ray (EDX) and Brunauer-Emmett-Teller (BET) method.

X-ray Diffraction (XRD)

X-ray crystallography is a method for determining the structure of crystalline solid. It relies on the relationship between density of materials and absorption of X-rays to discover information about the structure of crystalline materials. When X-rays bombard the crystal, electron in the atom will scatter with the degree of scattering proportional to the atomic number, *Z*. In a crystal, atoms lie in identical position so X-rays will be scatter in an identical manner. In that position, scattering pattern is amplified and it will be able to be detected.

In a modern instrument, the scattering pattern leads to diffraction patterns. From the diffraction pattern, the electron density of each atom can be reconstructed and identified using a computer. The bond length and bond length data can be determined in the computer but there is a limitation in order to locate hydrogen atoms that are close to heavier atoms since the scattering is proportional to *Z* (Burrows *et al.,* 2009).

According to English physicist William H.Bragg, the X-rays are diffracted by different layers of atoms causes' constructive interference in some instances but destructive interferences in others. By imaging incoming X-rays with wavelength λ strike a crystal face at an angle θ and then jump off the same angle. That rays strike an atom in the top layer is reflected at the same θ. But because the second layer of atoms is far from X-ray source, distance that the X-rays have to go to reach a second layer is far than the distance they have to go to reach the first layer by amount noted as *BC* in Figure 1.1 (Christian, 2004). .

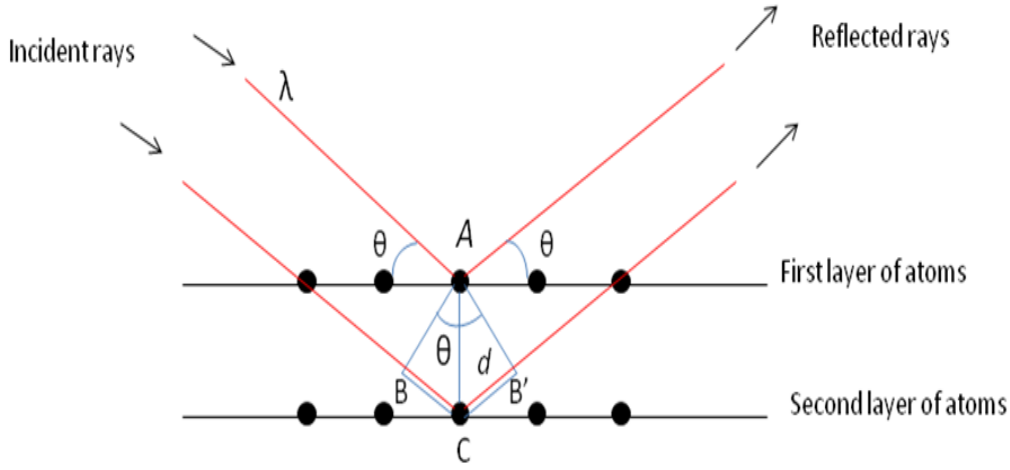

Figure 1.1: Diffraction of X-rays of wavelength λ from atoms in the top two layers of a crystal (Christian, 2004)

Distance *BC* is equal to the distance between atomic layers *d* (AC) times sin of the angle θ:

$$\sin \theta = BC/d$$

The extra distance *BC* = *CB* 'need to be travel by reflected rays as they exit crystals, making the distance $2d \sin \theta$. Extra distance also noted as $2d \sin \theta = n\lambda$ and arranging the equation to get *d* give Bragg equation:

$$BC = CB' = 2d \sin \theta = n\lambda$$

$$d = n\lambda / 2 \sin \theta$$

Field Emission Scanning Electron Microscopy (FESEM)

The field emission scanning electron microscopy was firstly discovered in 1942 and has been developed to the point where it can be routinely used for the highest resolution imaging. This instrument become very popular due to its emission gun is very small so that a probe of nanometer size with a very high brightness can be obtained. Compare to conventional tungsten filament gun, field emission gun has the smallest electron probes that allow 1000 times more amount of brightness (Goldstein *et al.*, 2007).

This instrument operating by a field-emission cathode in the electron gun of a scanning electron microscope provides narrower probing beams at low as well as high electron energy, resulting in both improved spatial resolution and minimized sample charging. Electrons generated by a field emission source are accelerated in a field gradient under vacuum condition. The beam passes through electromagnetic lenses and it will focus onto the specimen. As a result, this process cause bombardment with different types of electrons is emitted from the specimen. A detector will detect the secondary electrons and an image of the sample surface is constructed by comparing the intensity of the secondary electrons and the primary electron beam. Finally the image is displayed on a monitor.

These microscopes have found widespread application due to the images produces are clearer and less electrostatically distorted images with resolution down to 1 1/2 nm. Besides, FESEM can reduce the penetration of low kinetic energy electrons probes closer to the immediate material surface. High resolution and low beam energy capabilities are the reason why this instrument becomes popular in many field.

Energy Dispersive X-ray Spectroscopy (EDX)

During EDX Analysis, the sample is bombarded with an electron beam inside the scanning electron microscope. The bombarding electrons collide with the specimen atoms' own electrons, knocking some of them off in the process. The amount of energy released by the transferring electron depends on which shell it is transferring from. In addition, the atom of every element releases X-rays with certain amounts of energy during the transferring process. Thus, by measuring the amounts of energy present in the X-rays being released by a sample during electron beam bombardment, the identity of the atom can be determined.

Output of an EDX analysis is an EDX spectrum. The EDX spectrum is a plot of how frequently an X-ray is received for each energy level. An EDX spectrum will displays the peaks corresponding to energy levels for which the most X-rays had been received. Each of these peaks is unique to an atom, and therefore corresponds to a single element. The higher a peak in a spectrum, the more concentrated the element is in the specimen (Ingram *et al.*, 1999).

Brunauer- Emmett- Teller (BET) Method

Physisorption arises from the van der Waals forces. These forces will condense gas molecules into their liquid gas. Brunauer-Emmett-Teller developed theory in 1938 to describe physisorption, where the adsorbate thickness exceeds a monolayer. The original derivation of B.E.T of the B.E.T equation is an extension of Langmuir's treatment of monolayer adsorption from kinetics arguments. In B.E.T isotherm, it is assumed that: i) Adsorbate molecules will stay after adsorption. ii) Each first layer molecule acts as a potential adsorption site. The BET method is widely used in surface science for the determination of surface areas of solids by physical adsorption of gas molecules. In this study, nitrogen gas was used (Erbil, 2006).

iii) Characterization of electrochemical properties of Sn-Co-Cu, Sn-Co-Mn and Sn-Co- Fe

1.5 Significance of Research

This study was conducted to prepare ternary Sn-based alloy powders which are Sn-Co-Cu, Sn-Co-Mn and Sn-Co-Fe. Obtained products that enhance in structural and morphological study are possible to fulfill the high quality lithium ion batteries. The ternary Sn-based alloy powders are expected to have outstanding properties and provide great advantage for current anode replacement.

1.6 Thesis Outline

This thesis was divided into five chapters. Chapter 1 explained about the introduction of lithium ion battery and the important of its development which is the main reason for this research was carried out. Problem statement of the current research was stated to give the clear objectives of the study and the scope of the study covers to achieve this research objectives.

Chapter 2 or literature review covers development of lithium ion battery and the challenges to improve the current battery performance.tis chapter also covers how Sn has been selected as the alternative of anode electrode. The preparation methods of Sn-based materials were also mentioned and the performance of Sn-based as anode was highlighted.

Chapter 3 or experimental methodology describes the materials used in present work, the procedure of Sn- based alloy powders and anode preparation. This

chapter also includes the instrumentation that used for physical and electrochemical performance test.

In Chapter 4, results and discussion was divided into two parts, a) physical characterization b) electrochemical charge/discharge of the obtained alloy powders.

Finally, Chapter 5 covered the conclusions of the present study. Future studies and some recommendations are suggested in this chapter.

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