

SYNTHESIS OF VANADIUM BASED LITHIUM NICKEL ALUMINIUM OXIDE
SYSTEMS FOR GOOD PERFORMANCE CATHODE MATERIALS OF
LITHIUM-ION BATTERIES

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ABSTRACT

The objectives of this study is to synthesize lithium nickel oxide (LiNiO_2) systems doped with vanadium (V) and aluminium (Al) which gives a constant and good discharge capacity for several cycles. Due to that, $\text{LiNi}_{1-x-y}\text{Al}_y\text{O}_2$ systems were developed using carbon combustion synthesis (CCS) and solid-state reaction (SSR) method with different proportions ratio of V and Al which are $x = 0.1$ mole, and 0.3 mole and $y = 0.1$ mole. The sintering time used was 18 hours for SSR and five hours for CCS at 900°C . The first experiment is to obtain crystalline structure by x-ray diffraction analysis (XRD). The results revealed that the $\text{LiNi}_{1-x-y}\text{V}_x\text{Al}_y\text{O}_2$ are well defined hexagonal crystal system with $Rd3m$ space group. The morphology characterization was done by using scanning electron microscopy (SEM). The SEM image for CCS samples show the presence of hexagonal structures for all the materials and it also was homogeneous. The SEM image of SSR samples showed that the particles distribution were irregular in size and also inhomogeneous when more vanadium substituted in the samples. Energy dispersive of x-ray analysis (EDAX) was done to show the percentage ratio of metals synthesized and elements and it showed the desired result. The existence of impurities NO_3^- stretch appear at $1325\text{-}1450\text{ cm}^{-1}$ was confirmed from FTIR analysis. Lastly, electrochemical analysis has been done using cyclic voltammetry and charge/discharge. The cyclic voltammetry curves showed intercalation and deintercalation had occurred during testing for both methods. As conclusion, doping with vanadium and aluminium improves the discharge capacity of $\text{LiNi}_{0.8}\text{V}_{0.1}\text{Al}_{0.1}\text{O}_2$ which produced 80.57 mAh/g at the initial cycle and an average of 80.55 mAh/g for 10 cycles. The implication of this study show that doping method can improve the structural and electrochemical of the cathode materials of lithium-ion batteries.





SINTESIS BAGI SISTEM LITIUUM NIKEL ALUMINIUM OKSIDA BERASASKAN VANADIUM UNTUK BAHAN KATOD TERBAIK BAGI BATERI LITIUUM-ION

ABSTRAK

Objektif kajian adalah mensintesis sistem litium nikel oksida (LiNiO_2) yang ditusukkan dengan vanadium (V) dan aluminium (Al) dimana ia dapat menghasilkan kapasiti nyahcas yang berterusan dan bagus untuk beberapa kitaran. Sehubungan dengan itu, $\text{LiNi}_{1-x-y}\text{Al}_y\text{O}_2$ dibangunkan dengan kaedah pembakaran karbon (CCS) dan tindakbalas *solid-state* (SSR) dengan kandungan nisbah V dan Al yang berbeza iaitu $x = 0.1$ mol dan 0.3 mol, dan $y = 0.1$ mol. Masa pembakaran bagi kaedah SSR adalah 18 jam manakala pembakaran karbon adalah selama lima jam pada suhu 900°C . Ujikaji pertama adalah analisis struktur kristal ditentukan dengan *x-ray diffraction* (XRD). Keputusan menunjukkan $\text{LiNi}_{1-x-y}\text{Al}_y\text{O}_2$ mempunyai struktur kristal heksagon dengan kumpulan $R\bar{3}m$. Kriteria morfologi telah dilakukan dengan menggunakan *scanning electron microscopy* (SEM). Gambaran SEM bagi sampel-sampel CCS menunjukkan saiz butir adalah heksagon untuk ke semua sampel dan juga homogen. Bagi gambaran SEM bagi sampel-sampel SSR menunjukkan taburan partikel tidak begitu seragam dari segi saiz dan juga tidak homogen apabila pertambahan jumlah bahan vanadium. *Energy dispersive of x-ray* (EDAX) dilakukan untuk menunjukkan nisbah peratusan logam yang disintesis dan unsur yang dikehendaki. Kewujudan bendasing NO_3^- pada $1325\text{-}1450\text{ cm}^{-1}$ telah disahkan dari analisis FTIR. Akhir sekali analisis elektrokimia telah dilakukan menggunakan voltametri kitaran (CV) dan cas/nyahcas. Lengkungan voltametri kitaran telah menunjukkan berlakunya proses interkalasi dan deinterkalasi bagi kedua-dua kaedah. Kesimpulannya, penyusukan bahan vanadium dan aluminium telah meningkatkan nilai kapasiti nyahcas $\text{LiNi}_{0.8}\text{V}_{0.1}\text{Al}_{0.1}\text{O}_2$, iaitu 80.57 mAh/g pada kitaran awal dan 80.55 mAh/g untuk 10 kitaran purata. Implikasi kajian ini menunjukkan kaedah penyusukan dapat memperbaiki struktur dan elektrokimia bahan katod bateri litium ion.



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LIST OF ABBREVIATIONS

Al	Aluminium
Co	Cobalt
CV	Cyclic Voltammetry
CCS	Carbon Combustion Synthesis
EDAX	Energy Dispersive Analysis of X-Ray
EV	Electrical Vehicle
Fe	Iron
FCEVs	Fuel-Cell Electrical Vehicles
FTIR	Fourier Transform Infrared Spectroscopy
Ga	Gallium
HEVs	Hybrid Electrical Vehicles
IR	Infrared
LiNiO ₂	Lithium Nickel Oxide
LiCoO ₂	Lithium Cobalt Oxide
LiNiCoO ₂	Lithium Nickel Cobalt Oxide
LNMO/ LiNiMnO ₂	Lithium Nickel Manganese Oxide
LiNiAlO ₂	Lithium Nickel Aluminium Oxide
LiMn ₂ O ₄	Lithium Manganese Spinel
LiNiVO ₄	Lithium Nickel Vanadium Spinel Oxide
Li-ion	Lithium-Ion
LFP	Lithium Iron Phosphate
Mg	Magnesium
NiMH	Nickel Metal Hydride

Ni-Cd

Nickel Cadmium

NMR

Nuclear Magnetic Resonance Spectroscopy

PHEVs

Plug-in Hybrid Electrical Vehicles

RCB

Rocking Chair Batteries

SEM

Scanning Electron Microscopy

SEI

Solid-Electrolyte-Interface

SLI

Starting-Lighting-Ignition

SHS

Self-Propagating High-Temperature Synthesis

SSR

Solid-State Reaction

TEM

Transmission Electron Microscope

Ti

Titanium

V

Vanadium

XRD

X-Ray Diffraction

XAS

X-Ray Absorption Spectroscopy



CHAPTER 1

INTRODUCTION



1.1 Introduction

Battery is a device which is needed almost everywhere in this world as an alternative energy source compared to fossil fuel, nuclear energy, solar energy and etc. (Wakihara, 2001). According to Brain et.al, (2000):

Batteries are providing us with mobile sources of power that makes many modern conveniences possible. While there are many different types of batteries, the basic concept by which they function remains the same. When a device is connected to a battery, a reaction occurs that produces electrical energy

(Brain, Bryant, & Pumphrey, 2000, p. 1).





According to Linden & Reddy (2000), a battery known as an electrochemical cell and it is a device that converts the chemical energy contained in its active materials directly into electric energy by redox reaction (Linden & Reddy, 2002). On the other hand, Fox (1999) describes batteries as devices which comprised of one or more cells connected in series or parallel and assembled with terminal or contact. When these terminals are connected to a device electrical current flows through the completed circuit providing power (Fox, 1999).

1.1.1 History Related to Batteries

According to Brain et.al, (2000), early batteries was discovered in 1799:



An Italian physicist Alessandro Volta created the first battery by stacking

alternating layers of zinc, brine-soaked pasteboard or cloth, and silver. This arrangement, called a voltaic pile and it was not the first device to create electricity, but it was the first to emit a steady, lasting current. However, there were some drawbacks to Volta's invention. The height at which the layers could be stacked was limited because the weight of the pile would squeeze the brine out of the pasteboard or cloth. The metal discs also tend to corrode quickly, shortening the life of the battery. Despite these shortcomings, the SI unit of electromotive force is now called a volt in honour of Volta's achievement With the rise in portable devices such as laptops, cell phones, MP3 players and cordless power tools, the need for rechargeable batteries has grown substantially in recent years. Rechargeable batteries have been around since 1859 when French physicist Gaston Plante invented the lead-acid cell. With a lead anode,





a lead dioxide cathode and a sulfuric acid electrolyte, the Plante battery was a precursor to the modern-day car battery. (Brain et.al, 2000, pp. 2 - 4)

Rechargeable batteries and non-rechargeable batteries produce current exactly the same way which is through an “electrochemical reaction involving an anode, cathode, and electrolyte. In a rechargeable battery, the reaction is reversible and it is irreversible in a non-rechargeable battery. When electrical energy from an outside source is applied to a secondary cell, the negative-to-positive electron flow that occurs during discharge is reversed, and the cell's charge is restored. The most common rechargeable batteries on the market today are lithium-ion (Li-ion), though nickel-metal hydride (NiMH) and nickel-cadmium (Ni-Cd) batteries were also once very prevalent” (Brain et al., 2000, p. 4).



Brain et al (2000) found that among the batteries are created with a similar concept but, “not all the batteries are created equal” (p. 4). “Ni-Cd batteries were among the first widely available secondary cells, but they suffered from an inconvenient problem known as the memory effect. Basically, if these batteries were not fully discharged every time they were used, they would quickly lose capacity. Ni-Cd batteries were largely phased out in favour of NiMH batteries. These secondary cells boast a higher capacity and are only minimally affected by the memory effect, but they do not have a very good shelf life. On the other hand, Li-ion batteries have a long life, they hold the charge better, operate at higher voltages, and come in a much smaller and lighter package. Essentially all high-quality portable technology manufactured these days takes advantage of this technology. However, Li-ion batteries are not currently available in standard sizes such as AAA, AA, C or D, and they are considerably more





expensive than their older counterparts. For the Ni-Cd and NiMH batteries, charging can be tricky. The user has to be careful of not to overcharge them, as this could lead to decreased capacity. In order to prevent this from happening, some type of chargers switch to a trickle charge or simply shut off when charging is complete. Ni-Cd and NiMH batteries also must be reconditioned. The batteries should be completely discharged and recharge again every once in a while to minimize any loss of capacity. Li-ion batteries, on the other hand, have sophisticated chargers that prevent overcharging and they do not need reconditioning” (Brain et al., 2000, pp. 4-5).

1.1.2 Battery Chemical Reaction and Electrical Reactions in Batteries Reaction Chemistry



Batteries in the market have a few shape and sizes. We “will notice that it has two terminal which one terminal marked (+) or positive and the other is marked (-) or negative. The internal working of a battery is typically housed within a metal or plastic. Inside this case, they are consist of two electrically conductive electrodes, one positive (cathode) and the other one is negative (anode) combined with an electrolyte. A separator act as a barrier between the cathode and anode. This barrier is to prevent the electrodes from touching each other while allowing an electrical charge to flow freely between them. Reduction occurs at anode, which gives out electrons to an external circuit and it is oxidized during the electrochemical reaction. Oxidation occurs at the cathode, which accepts electrons from the external circuit and reduced during the electrochemical reaction. The electrolyte is an ionic conductor, which provides a medium for the ions to be transferred. This process occurs inside the cell between the anode and cathode electrodes. An electrolyte is typically a liquid such as molten salt,





acids or alkalis. Some batteries use solid electrolytes which are also ionic conductors at the operating temperature of the cell” (Brain et al., 2000, pp. 2-3).

In a battery system, a few factors were often discussed about their electrode combination such as energy and power density, discharge and temperature, stability, size weight, environmental effect, ease of manufacture, physical and safety (Fox, 1999).

1.1.3 Lithium Rechargeable Batteries

Lithium-ion batteries were commercialized in Japan in early 1991 whom supplied 90 percent of the total battery market (Wakihara, 2001). According to Hu et.al (2013),

“lithium ion-batteries have been widely used to portable electronic devices and more improvement in battery technology for extensive high energy density needed in electronic vehicles (EV), hybrid EVs (HEVs) and smart grids” (Hu, Pang, & Zhou, 2013, p. 229). Lithium-ion is a type of rechargeable batteries system, “the battery is recharged by a reversal of the process where the reaction process occurs when the electron is transferred from one material to another through an electrical circuit” (Linden, D & Reddy, 2002, p. 64).

1.1.4 Advantages of Lithium-Ion Batteries

Lithium is a very attractive material for high energy density batteries because of its elements which have low equivalent weight and high standard potential. In the periodic





table, lithium is located in group 1 (alkali metal) and it can oxidize very rapidly in air and water. Lithium is an essential component rechargeable batteries used almost ubiquitously in mobile gadgets such as phone, laptops, tablet, and computer and also in many electric vehicles (Qin et al, 2015). Brian (2006), described that “lithium-ion batteries are popular because of their important advantages over other batteries. The advantages are such as lighter than other types of rechargeable batteries because the electrodes are made of lithium and carbon. In addition, they have “no memory effect” which means that it does not have to be completely discharged before recharging it back and the cycle life is better”. (p. 1).

Lithium-ion batteries have attracted much attention in recent years because of their high energy density and long cycle life also. According to Väyrynen & Salminen (2012), “lithium-ion batteries are attractive rechargeable batteries which are the demand in the market due to their applications compared to the other rechargeable batteries. Lead-acid battery technology had been well proven for its performance and is more than a century old. However, the lead-acid battery shows low gravimetric and volumetric energy density. On the other hand, Nickel-metal hydride batteries provide reliable cyclability and are commonly used in hybrid vehicles. Their drawbacks are, relatively low energy density and low cycle life and relatively high self-discharge rate up to 10% per month”(Väyrynen & Salminen, 2012. p. 81). Figure 1.1 shows that lithium-ion batteries have the best potential compared with the other rechargeable batteries (Diouf & Pode, 2015).



1.2 Problem Statement

Lithium-ion batteries have a lot of advantages, however, lithium-ion batteries are flawed because they have few drawbacks due to that fact we cannot say lithium-ion has not fully mature yet and it is still improving. Stability issues (Yi et al, 2016) and degradation is the main factors influencing the battery performance especially on the cathode materials (Hausbrand et al., 2015).

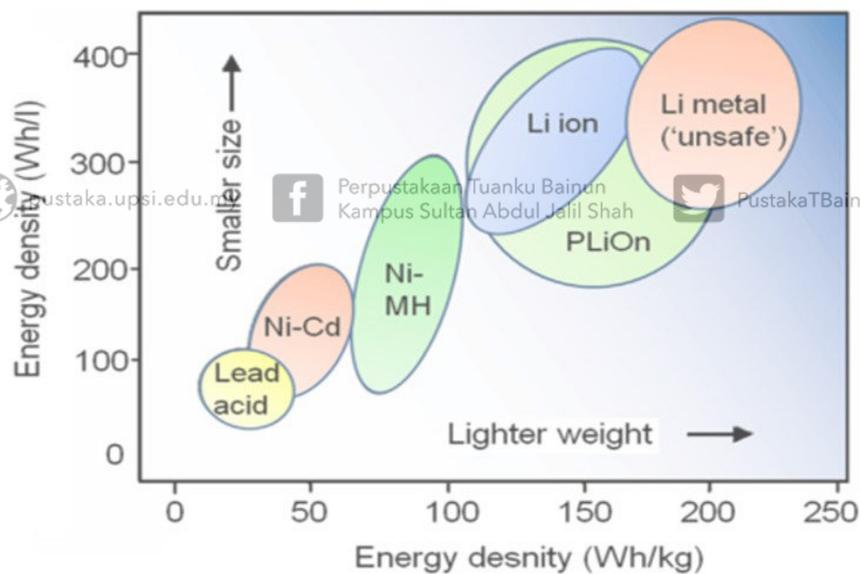


Figure 1.1. Comparison between Different Battery Technologies in Term of Volumetric and Gravimetric Densities. Reprinted from Issues And Challenges Facing Rechargeable Lithium Batteries. Nature, 414, p. 359 by Tarascon & Armand, 2001

According to Shering (2016), “the degradation and failure of Li-ion are strongly associated with the electrode microstructure change upon (de)lithiation”. (p. 16173). Even lithium-ion batteries which produce high potential energy, capacity fading occurs during charge-discharge processes. According to Madhavi et.al (2001),



the cause is due to the transformation of crystallographic phase and low thermal stability of the oxide in the charged state (Madhavi, Subba Rao, Chowdari, & Li, 2001). Wohfahrt et al (2004) stated that “capacity fading of cathode material can originate from three basic principles which are structural changes during cycling, chemical decomposition/dissolution reaction and surface modification”. (p. 59). In order to overcome the problem, “various strategies have been proposed such as doping, coating and fabricating porous micro/nano-structures” (Hu et al, 2015, p. 1). Doping has been considered to be used to improve the structure and electrochemical performance of the cathode material.

1.2.1 Vanadium Metal



Vanadium metal “has been the subject of much research for over 40 years due to their desirable physical properties” (McNulty et al., 2014, p. 834). According to Wang and Cao (2006), “it significantly enhanced intercalation properties for efficient energy storage and other device application”. (p. 2787). The intercalation refers to the “reversible intercalation of mobile guest species (atoms, molecules or ions) into a crystalline host lattice that contains an interconnected system of empty lattice sites of appropriate size, while the structural integrity of the host lattice is formally conserved. Guest materials may include metal ions, organic molecules, and organometallic molecules. When guest species are incorporated into host lattices, various structural changes can take place including a change in the interlayer spacing and the formation intermediate phases” (McNulty et al., 2014, p. 834).

