DISORDERED $LiNi_{0.5}Mn_{1.5}O_4$ SYNTHESIZED VIA MOLTEN SALT AND BALL-MILLING APPROACHES FOR HIGH VOLTAGE CATHODE IN LITHIUM-ION BATTERIES: MATERIALS CHARACTERISTICS AND ELECTROCHEMICAL PROPERTIES

NABILAH BINTI MOKHTAR

MASTER OF SCIENCE

UNIVERSITI MALAYSIA TERENGGANU

2017

DISORDERED $LiNi_{0.5}Mn_{1.5}O_4$ SYNTHESIZED VIA MOLTEN SALT AND BALL-MILLING APPROACHES FOR HIGH VOLTAGE CATHODE IN LITHIUM-ION BATTERIES: MATERIALS CHARACTERISTICS AND ELECTROCHEMICAL PROPERTIES

NABILAH BINTI MOKHTAR

Thesis Submitted in Fulfillment of the Requirement for the Degree of Master of Science in the School of Ocean Engineering

Universiti Malaysia Terengganu

February 2017

Abstract of this thesis presented to the Senate of Universiti Malaysia Terengganu in fulfillment of the requirement for the degree of Master of Science

DISORDERED $LiNi_{0.5}Mn_{1.5}O_4$ SYNTHESIZED VIA MOLTEN SALT AND BALL-MILLING APPROACHES FOR HIGH VOLTAGE CATHODE IN LITHIUM-ION BATTERIES: MATERIALS CHARACTERISTICS AND ELECTROCHEMICAL PROPERTIES

NABILAH BINTI MOKHTAR

February 2017

Main Supervisor : Nurul Hayati Binti Idris, Ph.D.

School : School of Ocean Engineering

$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) has been successfully synthesized via molten salt and ball-milling methods using three different types of precursors, which is acetate, carbonate, and chloride. The powders obtained from both methods were annealed at the temperatures of 750, 850 and 950 °C; respectively for 12 hours. The structure and morphology of the LNMO were characterized using X-ray diffraction (XRD), scanning electron microscope, and high-resolution transmission electron microscope (HRTEM). The XRD patterns of all samples can be indexed to *Fd3m* space group (Joint Committee on Powder Diffraction Standards-card no: 80-2162). The samples formed a polyhedral shape with particles sizes, ranging between 0.5 and 7.0 µm for LNMO synthesized from molten salt method, while for the LNMO prepared from ball-milling method the particle sizes were ~ 0.1 – 5.0 µm. The HRTEM results show the *d*-spacing of the lattice fringes measured was 0.24 nm and consistent with the characteristics plane (311) of LNMO for space group of *Fd3m*. Next, galvanostatic charge-discharge and cyclic voltammetry were performed for evaluate the electrochemical performances of the LNMO. For

molten salt method, the highest electrochemical performance was obtained by the LNMO sample when synthesized using carbonate precursor at the annealing temperature of 850 °C. This LNMO electrode delivers high initial discharge capacity of 122 mAh g^{-1} at 0.2 C rate and retained 91 % of its capacity after 100^{th} cycles. While, for ball-milling method, excellent electrochemical performances was exhibited by the LNMO prepared using carbonate precursor and annealed at the temperature of 750 °C. This LNMO exhibits the highest discharge capacity with the initial discharge capacity of 131 mAh g^{-1} at 0.2 C rate and retained its capacity about 88 % after 100^{th} cycle. Moreover, both electrodes show a good rate capability when exposed to different rates. Excellent electrochemical characteristics of these samples can be explained through their high crystallinity, homogeneity, and morphology which help to improve their performance. High crystallinity of the samples are beneficial for cyclability and enhance the discharge capacity, while small particle size of the sample could provides large surface area and shorten the diffusion path of the Li^{+} during charge-discharge. As a conclusion, this LNMO is a potential candidate to be a cathode material for Li-ion battery due the high performance of the materials.

Abstrak tesis ini disediakan untuk Senat Universiti Malaysia Terengganu sebagai memenuhi keperluan untuk Ijazah Sarjana Sains

KETIDAKATURAN $LiNi_{0.5}Mn_{1.5}O_4$ DISINTESIS MELALUI PENDEKATAN GARAM LEBUR DAN KISARAN BOLA BAGI KATOD BERVOLTAN TINGGI DALAM BATERI LITIUM-ION: CIRI-CIRI BAHAN DAN SIFAT ELEKTROKIMIA

NABILAH BINTI MOKHTAR

Februari 2017

Penyelia Utama : Nurul Hayati Binti Idris, Ph.D.

Pusat Pengajian : Pusat Pengajian Kejuruteraan Kelautan

$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) telah berjaya dihasilkan menggunakan kaedah sintesis garam lebur dan kisaran bola menggunakan tiga jenis prekursor iaitu asetat, karbonat dan klorida. Sampel yang terhasil daripada kedua-dua kaedah telah dipanaskan pada suhu 750, 850 dan 950 °C masing-masing untuk 12 jam. Pencirian struktur dan morfologi LNMO telah dilakukan menggunakan pembelauan sinar-X (XRD), mikroskop imbasan elektron dan mikroskop hantaran elektron resolusi tinggi (HRTEM). Paten XRD untuk semua sampel dikelaskan pada kumpulan *Fd3m* (Gabungan Kumpulan Piawaian Serbuk Pembelauan-kad nombor: 80-2162). Sampel ini membentuk bentuk polihedron dengan saiz partikel berkadar antara 0.5 dan 7.0 µm bagi LNMO disintesis daripada kaedah garam lebur, manakala untuk LNMO yang disintesis daripada kaedah kisaran bola, saiz partikel adalah ~0.1 – 5.0 µm. Manakala, keputusan HRTEM menunjukkan jejari *d*-langkau berukuran 0.24 nm dan konsisten dengan ciri satah (311) LNMO pada kumpulan *Fd3m*. Galvanostatik cas-discas dan kitaran voltammetri dilakukan bagi

menilai pencapaian elektrokimia LNMO. Bagi kaedah sintesis garam lebur, nilai elektrokimia tertinggi diperolehi oleh sampel LNMO disintesis menggunakan prekursor karbonat yang dipanaskan pada suhu 850 °C. Elektrod LNMO ini menghasilkan kapasiti discas iaitu 122 mAh g^{-1} pada kadar 0.2 C dan mengekalkan kapasiti pada nilai 91 % selepas kitaran yang ke 100. Manakala untuk kaedah kitaran bola, nilai terbaik elektrokimia dihasilkan oleh LNMO menggunakan prekursor karbonat dan dipanaskan pada suhu 750 °C. LNMO ini menghasilkan nilai kapasiti tertinggi dengan permulaan discas kapasiti 131 mAh g^{-1} pada kadar 0.2 C dan mengekalkan kapasiti pada nilai 88 % selepas kitaran ke 100. Tambahan pula, kedua-dua elektrod menunjukkan kadar keupayaan yang baik apabila didedahkan pada kadar berbeza. Ciri elektrokimia terbagus yang dihasilkan oleh sampel ini boleh dijelaskan berikutan ketinggian kristal, kesamarataan dan morfologi yang membantu meningkatkan pencapaian. Ketinggian kristal oleh sampel bagus untuk kitaran dan meningkatkan kapasiti discas, manakala saiz partikel yang kecil menyediakan ruang permukaan yang besar dan memendekkan jarak penyerapan Li^{+} semasa cas-discas. Kesimpulannya, LNMO ini adalah calon berpotensi untuk menjadi katod bagi bateri Li-ion berdasarkan kepada pencapaian yang bagus bagi bahan ini.