COMPARATIVE SYNTHESIS METHODS OF DISORDERED $LiNi_{0.5}Mn_{1.5}O_4$ SPINEL AS A LITHIUM-ION BATTERY'S CATHODE FOR HIGH ENERGY DENSITY APPLICATIONS

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ABSTRACT

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

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$LiNi_{0.5}Mn_{1.5}O_4$ has been successfully synthesized by glycine-assisted solution route at low-temperature reaction, ball-milling, and ionic liquid-assisted rheological phase body reaction method, followed by thermal treatments at 750, 850, and 950 °C, respectively for 12 h. The X-ray diffraction patterns of all samples can be assigned to a cubic spinel $LiNi_{0.5}Mn_{1.5}O_4$ with *fd3m* space group (Joint Committee on Powder Diffraction Standards-card no: 80-2162). From the transmission electron microscope images, the *d*-spacing between the lattice fringes is approximately 0.47 nm and consistent with the characteristic plane (111) of *fd3m* for $LiNi_{0.5}Mn_{1.5}O_4$. For $LiNi_{0.5}Mn_{1.5}O_4$ synthesized via glycine-assisted solution route at low-temperature reaction, pure phase of $LiNi_{0.5}Mn_{1.5}O_4$ was obtained for sample S750 and S850, while NiO peaks are arises in sample S950. From the scanning electron microscopy observations, these samples were composed of polyhedron shape with particle sizes in the range of 3.52 to 4.46 μm. The electrochemical results indicate that S750 electrode delivers the highest discharge capacity of 110 mAh g^{-1} at 0.2 C rate after 100 cycles. The electrode also exhibits good rate capability when exposed to

different rates, which is 104, 98, 94, and 90 mAh g^{-1} at 0.2, 0.4, 0.6, 0.8 and 1 C, respectively. For the $LiNi_{0.5}Mn_{1.5}O_4$ prepared through ball-milling method, all samples contain NiO as a impurity, and exhibits a polyhedral morphology with a particle sizes ranging from 0.88 and 3.33 μm. B750 electrode exhibited the highest discharge capacity of 89 mAh g^{-1} at 0.2 C rate. Moreover, this electrode delivers the highest discharge capacities of 100, 94, 89, and 86 mAh g^{-1} at a rate of 0.4, 0.6, 0.8, and 1 C. While, for the $LiNi_{0.5}Mn_{1.5}O_4$ prepared using ionic liquid-assisted rheological phase reaction, NiO as an impurity were detected in all samples and formed a well-polyhedral shape, ranging between 3.44 and 6.41 μm in size. R750 electrode possesses the highest discharge capacity of 66 mAh g^{-1} at 0.2 C rate after 100 cycles and exhibited a discharge capacities of 76, 74, 71, and 69 mAh g^{-1} at a rate of 0.4, 0.6, 0.8, and 1 C. For cyclic voltammetry, S750, B750, and R750 electrodes has a larger reduction peaks at 4.6 V which relate to the Ni^{2+}/Ni^{3+} redox peak, while the small peak at around 3.8 V was associated with Mn^{3+}/Mn^{4+}. As a conclusion, all $LiNi_{0.5}Mn_{1.5}O_4$ samples annealed at 750 °C exhibits the highest electrochemical performances. Specifically, the highest electrochemical performances can be achieved by the $LiNi_{0.5}Mn_{1.5}O_4$ synthesized via glycine-assisted solution route at low-temperature reaction due to the small particle size of the sample, by providing a large surface area, thus can accelerates the lithium intercalation/de-intercalation kinetics during cycling.

ABSTRAK

Abstrak tesis yang dikemukakan kepada Senat Universiti Malaysia Terengganu sebagai memenuhi keperluan untuk ijazah Sarjana Sains

PERBANDINGAN KAEDAH SINTESIS TERHADAP KETIDAKATURAN $LiNi_{0.5}Mn_{1.5}O_4$ SPINEL SEBAGAI KATOD BATERI LITIUM-ION UNTUK APLIKASI TENAGA BERKETUMPATAN TINGGI

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$LiNi_{0.5}Mn_{1.5}O_4$ telah berjaya dihasilkan menggunakan kaedah laluan larutan glycine dibantu reaksi suhu rendah, kisaran bola, dan cecair bantuan ionik reaksi fasa reologi, diikuti dengan rawatan haba pada suhu 750, 850, dan 950 °C untuk 12 jam. Paten pembelauan X-ray untuk semua sampel dikelaskan pada kumpulan *fd3m* (gabungan kumpulan piawaian serbuk pembelauan-kad nombor: 80-2162). Berdasarkan imej mikroskop hantaran elektron, *d*-langkau di antara jejari adalah 0.47 nm dan konsisten dengan ciri satah (111) $LiNi_{0.5}Mn_{1.5}O_4$ pada kumpulan *fd3m*. Bagi $LiNi_{0.5}Mn_{1.5}O_4$ disintesis melalui laluan larutan glycine dibantu reaksi suhu rendah, sampel S750 dan S850 memperolehi fasa tulen $LiNi_{0.5}Mn_{1.5}O_4$, manakala terdapat puncak NiO telah timbul dalam sampel S950. Daripada pemerhatian mikroskop imbasan elektron, sampel ini terdiri daripada bentuk polihedron dengan saiz partikel dalam julat 3.52-4.46 μm. Keputusan elektrokimia menunjukkan bahawa elektrod S750 menyampaikan kapasiti discas yang tertinggi iaitu 110 mAh g^{-1} pada kadar 0.2 C selepas 100 kitaran. Elektrod ini juga menghasilkan keupayaan kadar yang baik apabila didedahkan pada kadar yang berbeza, iaitu 104, 98, 94, dan 90 mAh g^{-1} pada

0.2, 0.4, 0.6, 0.8 dan 1 C. Bagi $LiNi_{0.5}Mn_{1.5}O_4$ disintesis melalui kaedah kisaran bola, semua sampel mengandungi NiO sebagai bendasing, dan mempamerkan morfologi polihedral dengan saiz partikel antara 0.88 dan 3.33 μm. Elektrod B750 menghasilkan nilai kapasiti discas tertinggi iaitu 89 mAh g^{-1} pada kadar 0.2 C. Selain itu, elektrod ini menyampaikan nilai kapasiti discas tertinggi iaitu 100, 94, 89, dan 86 mAh g^{-1} pada kadar 0.4, 0.6, 0.8, dan 1 C. Manakala, untuk $LiNi_{0.5}Mn_{1.5}O_4$ yang disintesis daripada kaedah cecair bantuan ionik reaksi fasa reologi, NiO sebagai bendasing dapat dikesan di dalam semua sampel dan membentuk bentuk polihedral dengan saiz partikel berkadar antara 3.44 dan 6.41 μm. Elektrod R750 mempunyai nilai kapasiti discas tertinggi iaitu 66 mAh g^{-1} pada kadar 0.2 C selepas 100 kitaran dan menghasilkan nilai kapasiti discas tertinggi iaitu 76, 74, 71, dan 69 mAh g^{-1} pada kadar 0.4, 0.6, 0.8, dan 1 C. Untuk kitaran voltammetri, elektrod S750, B750, dan R750 mempunyai puncak yang lebih besar pada 4.6 V yang berkaitan dengan puncak redok Ni^{2+}/ Ni^{3+}, manakala puncak kecil sekitar 3.8 V yang dikaitkan dengan Mn^{3+}/Mn^{4+}. Sebagai kesimpulan, semua sampel $LiNi_{0.5}Mn_{1.5}O_4$ yang dipanaskan pada suhu 750 °C menunjukkan nilai elektrokimia tertinggi. Khususnya, prestasi elektrokimia tertinggi boleh dicapai oleh $LiNi_{0.5}Mn_{1.5}O_4$ yang disintesis melalui kaedah laluan larutan glycine dibantu reaksi suhu rendah disebabkan oleh saiz partikel yang kecil dengan menyediakan ruang permukaan yang besar, dengan itu boleh mempercepatkan kinetik interkalasi/de-interkalasi litium semasa kitaran.