UNIVERSITI TEKNOLOGI MARA

SYNTHESIS OF NANOSTRUCTURED CATHODE MATERIALS FOR LI-ION BATTERY

ROSHIDAH BINTI RUSDI

PhD

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AUTHOR'S DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Teknologi MARA. It is original and is the results of my own work, unless otherwise indicated or acknowledged as referenced work. This thesis has not been submitted to any other academic institution or non-academic institution for any degree or qualification.

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Name of Student	:	Roshidah Binti Rusdi
Student I.D. No.	:	2012999319
Programme	:	Doctor of Philosophy – AS950
Faculty	:	Applied Sciences
Thesis	:	Synthesis of Nanostructured Cathode Materials for Li-ion Battery
Signature of Student	:	……..
Date	:	December 2020

ABSTRACT

Two types of lithium transition metal oxides, namely Lithium Nickel Cobalt Oxide ($LiNi_{1-x}Co_xO_2$), and Lithium Nickel Cobalt Titanium Oxide ($LiNi_{0.7-z}Co_{0.3}Ti_zO_2$), were successfully synthesized using the modified combustion method. Stoichiometric and overlithiated samples were prepared. The overlithiated samples for both are overlithiation of Lithium Nickel Cobalt Oxide ($Li_{1+y}Ni_{1-x}Co_xO_2$), and overlithiation of Lithium Nickel Cobalt Titanium Oxide ($Li_{1+y}Ni_{0.6}Co_{0.3}Ti_{0.1}O_2$ and $Li_{1+y}Ni_{0.6-y}Co_{0.3}Ti_{0.1}O_2$). Simultaneous Thermogravimetric Analysis (STA) were done on the parent samples $LiNi_{1-x}Co_xO_2$ to study the thermal properties and decomposition of the precursors and to identify the right annealing temperature for parent and all modified compounds. The precursors were later heated for 24, 48 and 72 h at 700 °C. This is done to study the effect of annealing time on the characteristics of the materials as well as to get the optimum annealing temperature for good battery performance. X-Ray Diffractions of the samples were taken to confirm the identity of the materials and to determine the purity of the products. XRD results showed that the materials were all single phase with hexagonal layered structure of *R*-3*m* space group. The morphology of the materials and the crystallite size of the materials were determined using Field Emission Scanning Electron Microscopy (FESEM). Results show that the polyhedral like morphology of $LiNi_{1-x}Co_xO_2$ obtained have particles in micron size while polyhedral morphology of $LiNi_{0.6}Co_{0.3}Ti_{0.1}O_2$ is in the form of plate-like crystals in nano-size (between 41 to 81 nm). Elemental analysis carried out using Energy Dispersive X-ray Spectroscopy (EDX) proved all synthesized materials have the stoichiometric ratio as calculated. Fabrication of the cathodes and assembling of the batteries were done to study the electrochemical properties. Overall performance show the best stoichiometry for $LiNi_{1-x}Co_xO_2$ is $LiNi_{0.7}Co_{0.3}O_2$. This compound is further improved by partial substitution with Ti producing $LiNi_{0.7-z}Co_{0.3}Ti_zO_2$ materials. The best stoichiometry with the best electrochemical performance for $LiNi_{0.7-z}Co_{0.3}Ti_zO_2$ group is $LiNi_{0.6}Co_{0.3}Ti_{0.1}O_2$ which is further improved by overlithiation is shows the interstitially doped Li material has better performance than substitutionally doped material. The specific capacity of the $LiNi_{0.6}Co_{0.3}Ti_{0.1}O_2$ is in the range of 141.6 to 146.0 mAh/g with a small capacity fading of 8.2% to 12.7% after cycling 70th cycle. The results are improved as compared to lab measurement of commercial $LiCoO_2$ which is about 120 mAh/g for the first cycle. All the best stoichiometry were then subjected to in-depth study for crystal structure using the Rietveld refinement method, crystallite size studies using TEM and oxidation state studies using X-ray Photoelectron Spectroscopy (XPS). The relationship between the structure, oxidation state and the electrochemical performance were studied to deeply understand on why the material shows good electrochemical behaviour and performance. It was found that the oxidation state of the transition metals play an important role in cycleability of materials. The structural study also found that the side occupancy factor, cell parameter, cell structure and the stoichiometric amount of each transition metal in each structural site also influence the electrochemical performance. Therefore, this research was able to explain as to why the material shows good performance in terms of specific capacity and cycleability.

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