# UNIVERSITI TEKNOLOGI MARA

# SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMICAL INVESTIGATION OF $LiMn_{1.9}Ti_{0.1-x}Sn_xO_4$ SPINEL CATHODE MATERIALS FOR LITHIUM-ION BATTERIES

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Thesis submitted in fulfillment
of the requirements for the degree of
**Doctor of Philosophy**
**(Physics)**

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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.

I, hereby, acknowledge that I have been supplied with the Academic Rules and Regulations for Post Graduate, Universiti Teknologi MARA, regulating the conduct of my study and research.

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# ABSTRACT

Spinel $LiMn_{1.9}Ti_{0.1}O_4$ compound faces large capacity fading when the charge and discharge cycle is repeated. Due to this drawback, its structural and morphological properties as well as its electrochemical performance may be improved by doping. In this work, doping of $LiMn_{1.9}Ti_{0.1}O_4$ with Tin (Sn) is done by using two methods which are the sol-gel method (SG) and self-propagation combustion method (SPC). The drive for this research is to obtain pure and single phase structure as well as optimising the annealing temperature. Thus, 700°C and 800°C were chosen. This study also focuses in improving the specific capacity and increase the capacity retention of batteries with these doped materials compared to $LiMn_{1.9}Ti_{0.1}O_4$. Synthesizing using the SG method resulted in impurities of $Mn_2O_3$ and $Mn_3O_4$ for samples annealed at 700°C and 800°C, respectively. Contradicting, the SPC method gives a single and pure phase materials. Thus, the fundamental properties such as thermal behaviour and crystal structure, particle size, morphology and battery performance of samples synthesized by SPC method were studied in depth. The thermal properties of these materials were studied by Simultaneous Thermogravimetric Analysis (STA) to determine suitable annealing temperature for phase formation. The annealing temperature for $LiMn_{1.9}Ti_{0.1}O_4$ with its doped materials, $LiMn_{1.9}Ti_{0.1-x}Sn_xO_4$ (x = 0.001, 0.002, 0.003, 0.004 and 0.005) material were chosen based on the thermal profile of the samples. The phases for all the materials were studied by X-Ray Diffraction (XRD). XRD revealed that all samples annealed at 700 and 800 $^oC$ for 24 h showed pure and single phase. According to FESEM results, the morphologies obtained were polyhedral type crystal and the crystallite size increased as the ratio of Sn increases. EDX results showed that the calculated stoichiometry were in good agreement with the experimental errors of less than 15.0 %. The cyclic voltammetry (CV) results showed oxidation loop at potential more than 3.5 V. As such, doped $LiMn_{1.9}Ti_{0.1-x}Sn_xO_4$ materials progress as good candidates for cathode materials. Of all the samples obtained, $LiMn_{1.9}Ti_{0.099}Sn_{0.001}O_4$ material has the best specific discharge capacity of 156.7 $mAhg^{-1}$ in the first cycle, with capacity retention after $50^{th}$ cycle of 69.0 %. Thus, $LiMn_{1.9}Ti_{0.099}Sn_{0.001}O_4$ material has potential as cathode material for use in lithium-ion batteries.

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