



**SYNTHESIS OF LITHIUM MANGANESE OXIDE/GRAPHENE  
NANOPLATELETS NANOCOMPOSITE FOR AQUEOUS  
SUPERCAPATTERY**

**By**

**LOW JO RING**

**Thesis Submitted to the School of Graduate Studies, Universiti Putra  
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Science**

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

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**DECEMBER 2022**

**Chair : Lim Hong Ngee, PhD**  
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The low energy density of supercapacitor and low power density of lithium-ion batteries limits its real-life application. Supercapattery is an innovative hybrid energy storage device, which combines the merits of rechargeable batteries and supercapacitors into a single device. Spinel-structured lithium-manganese oxide (LMO) cathode material is one of the intriguing energy storage material due to its low cost and low toxicity. Besides, it has been successful commercialized for large scale energy storage, but its low conductivity and stability resulting in fast capacity fading. Composites of LMO nanoparticles in a graphene matrix can be used to compensate their low conductivity. In addition, synthesis methodology of LMO plays an important duty to improve the power and energy density of a supercapattery as it affects the electrochemical properties of the LMO cathode. Herein, lithium manganese oxide/graphene nanoplatelets (LMO/GNPs) composite was synthesized by both hydrothermal (HT) and solid-state reaction (SSR) methods to investigate the effect of preparation methods on the physicochemical properties and electrochemical behavior of the composite as the cathode for supercapattery applications. This cathode is characterized by different physicochemical techniques to analyze the structure of crystalline materials, surface area, and morphology of the composites such as FE-SEM, N<sub>2</sub> absorption and desorption, XRD, and Raman spectroscopy. Meanwhile, the electrochemical performance of the fabricated cathode is evaluated within a Swagelok cell with GNPs as an anode, in an eco-friendly and safer aqueous electrolyte of 1 M Li<sub>2</sub>SO<sub>4</sub>. Nylon membranes were soaked in the aqueous electrolyte to act as the separator to separate the anode and cathode physically and facilitate the lithium-ion transportation in the cell. LMO/GNPs prepared via the HT approach are found to provide a well-distribution of nanometer-size particles and enhance the specific surface area, which led to an improvement in electrochemical properties compared to the SSR method. The assembled supercapattery of h-LMO has achieved the specific capacity and capacitance of 26.2 mA h g<sup>-1</sup> and 191.98 F g<sup>-1</sup>. Interestingly, the incorporation of 1 mg GNPs on

the surface of LMO by the HT method led to a 70% increase in specific capacitance and initial discharge capacity. H-LMO/GNPs<sub>1</sub> exhibits a high energy density and power density of 39.07 W h kg<sup>-1</sup> at 925.40 W kg<sup>-1</sup>, respectively. This is due to the high conductive properties of GNPs that promote faster electron transfer kinetics for efficient Li<sup>+</sup> diffusion. Improved cycle stability of 82% capacity retention for over 1000 consecutive cycles is obtained for h-LMO/GNPs<sub>1</sub> based cathode. Ultimately, the method of preparing LMO/GNPs composites showed great influence on the surface chemistry, surface area, and the resulting supercapattery performance.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia  
sebagai memenuhi keperluan untuk ijazah Master Sains

## **SINTESIS NANOKOMPOSIT LITIMUM MANGAN OKSIDA/ NANOPATELET GRAFIN UNTUK SUPERKAPATERI AKUEUS**

Oleh

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Tenaga ketumpatan yang rendah dari superkapasitor dan ketumpatan kuasa rendah dari litium ion menghadkan aplikasi dalam kehidupan sebenar. Superkapateri merupakan satu peranti hibrid penyimpanan tenaga yang berinovatif dengan menggabungkan kelebihan bateri dan superkapasitor. Bahan katod struktur-spinel litium mangan oksida (LMO) adalah salah satu bahan tenaga simpanan yang menarik disebabkan kos dan toksikiti yang rendah. Selain itu, konduktiviti dan kestabilan litium mangan oksida yang rendah menyebabkan kepudaran kapasiti dengan cepat walaupun ia telah berjaya dikomersialkan untuk simpanan tenaga berskala besar. Komposisi LMO nanozarah yang mengandungi matrik grafin boleh digunakan untuk mengimbangi kekonduksiannya yang rendah. Tambahan pula, kaedah untuk mensintesis LMO memainkan peranan yang penting untuk meningkatkan ketumpatan kuasa dan tenaga superkapateri kerana ia akan memberi kesan kepada sifat elektrokimia kepada katod LMO. Di sini, komposit litium mangan oksida/grafin nanoplatelet (LMO/GNPs) telah dihasilkan melalui dua kaedah iaitu hidroterma (HT) dan tindak balas keadaan pepejal (SSR) untuk mengkaji kesan kaedah penyediaan ke atas sifat-sifat fizikokimia dan kelakuan elektrokimia terhadap komposit tersebut yang berperanan sebagai katod untuk aplikasi superkapateri. Katod ini diuji oleh teknik fizikokimia yang berbeza seperti FE-SEM, penyerapan N<sub>2</sub>, XRD dan spektroskopi raman untuk menganalisis struktur bahan kristal, luas permukaan dan morfologi komposit. Prestasi elektrokimia katod yang telah disintesis akan dinilai dalam sel Swagelok dengan GNP sebagai anod dengan kehadiran elektrolit berasaskan akueus yang mesra alam dan lebih selamat seperti 1 M Li<sub>2</sub>SO<sub>4</sub>. Membran nilon akan direndamkan dalam elektrolit dan bertindak sebagai pemisah untuk memisahkan katod dengan anod. Selain itu, pemisah ini juga akan memudahkan pengangkutan ion dalam sel. Komposit LMO/GNPs yang disediakan melalui pendekatan HT telah dibuktikan bahawa ia dapat meningkatkan taburan zarah bersaiz nanometer dengan cekap

dan meningkatkan luas permukaan spesifik. Maka, komposit ini mampu meningkatkan sifat elektrokimia berbanding dengan kaedah SSR. Superkapateri yang dipasangkan dengan h-LMO sebagai katod telah mencapai kapasiti dan kapasitan spesifik yang tinggi iaitu  $26.2 \text{ mA h g}^{-1}$  dan  $191.98 \text{ F g}^{-1}$ . Malah, penambahan  $1 \text{ mg GNP}$  pada LMO membawa kepada peningkatan sebanyak  $70\%$  untuk kapasitan spesifik dan kapasiti nyahcas awal. Di samping itu, h-LMO/GNPs<sub>1</sub> telah mendapatkan ketumpatan tenaga dan kuasa yang tinggi sehingga  $39.07 \text{ W h kg}^{-1}$  dan  $925.40 \text{ W kg}^{-1}$ . Hal ini disebabkan oleh sifat GNP yang berkonduktif tinggi telah menggalakkan kinetik pemindahan elektron dengan lebih pantas untuk mendapatkan resapan  $\text{Li}^+$  yang efisien. Selain itu, peningkatan kestabilan kitaran sebanyak  $82\%$  pengekal kapasiti bagi lebih  $1000$  kitaran secara berturut-turut diperoleh katod yang berasaskan h-LMO/GNPs<sub>1</sub>. Justeru itu, kaedah penyediaan komposit LMO/GNPs menunjukkan pengaruh yang besar terhadap kimia permukaan, luas permukaan serta prestasi superkapateri yang terhasil.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of science. The members of the Supervisory Committee were as follows:

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## LIST OF ABBREVIATIONS

0D	Zero-dimensional
3D	Three-dimensional
AC	Activated carbon
Al	Aluminium
Ar	Argon
BET	Brunauer, Emmett, and Teller
CNF	Carbon nanofiber
$\text{Co}_{0.5}\text{Mn}_{0.5}\text{S}$	Cobalt manganese sulfide
$\text{CO}_2$	Carbon dioxide
$\text{Co}_3(\text{PO}_4)_2$	Cobalt (II) phosphate
$\text{Co}_3\text{O}_4$	Cobalt oxide
$\text{CoO}_2$	Oxido(oxo)cobalt
$C_T$	Specific capacitances
CV	Cyclic voltammetry
D	Lithium-ion diffusion coefficient
DI	Deionized
E	Specific energy density
EDLC	Electric double layer capacitor
EDX	Energy dispersive X-ray
EES	Electrochemical energy storage
EIS	Electrochemical impedance spectroscopy
$\text{Fe}_2\text{O}_3$	Ferric Oxide / Iron (III) oxide
$\text{Fe}_3\text{O}_4$	Iron (II, III) oxide
$\text{FeCoCuS}_2$	Iron-cobalt-copper disulfide

FeF <sub>2</sub>	Iron (II) fluoride
FESEM	Field emission scanning electron microscopy
GCD	Galvanostatic charge-discharge
GNP	Graphene nanoplatelets
H <sub>2</sub> O	Water vapor
HT	Hydrothermal method
KMnO <sub>4</sub>	Potassium permanganate
l	Lithium-ion diffusion distance
LCO	Lithium cobalt oxide
LFP	Lithium iron phosphate
Li <sup>+</sup>	Lithium-ion
Li <sub>2</sub> CO <sub>3</sub>	Lithium carbonate
Li <sub>2</sub> MnSiO <sub>4</sub>	Lithium manganese silicate
Li <sub>2</sub> SO <sub>4</sub>	Lithium sulfate
Li <sub>2</sub> TiSiO <sub>5</sub>	Titanium silicate lithium
LiBF <sub>4</sub>	Lithium tetrafluoroborate
LiOH	Lithium hydroxide
LiTFSI	Lithium bis(trifluoromethane sulfonyl)imide
LMO	Lithium manganese oxide
LNO	Lithium nickel oxide
LTO	Lithium Titanate
Mn <sub>3</sub> O <sub>4</sub>	Manganese oxide
β-MnO <sub>2</sub>	Beta-Manganese dioxide
N <sub>2</sub>	Nitrogen
Na <sub>2</sub> SO <sub>4</sub>	Sodium sulfate
Ni <sub>0.75</sub> Mn <sub>0.25</sub> (PO <sub>4</sub> ) <sub>2</sub>	Nickel-manganese phosphates

NiCoAl	Nickel cobalt aluminum
NiFe-P	Nickel Iron phosphate
NiMnO <sub>4</sub>	Nickel molybdate
NiO	Nickel oxide
NMP	N-Methyl-2-Pyrrolidone
P	Specific power density
PVDF	Polyvinylidene fluoride
Q	Specific capacity
R <sub>ct</sub>	Resistance of charge transfer
rGO	Reduced graphene oxide
R <sub>s</sub>	Resistance of solution
SEI	Solid electrolyte interface
SmCoO <sub>3</sub>	Samarium cobalt oxide
SSA	Specific surface area
SSR	Solid state reaction
t	Lithium-ion diffusion time
WiS	Water in salts
XRD	X-ray diffraction
Zn <sub>0.5</sub> Co <sub>0.5</sub> S	Zinc cobalt sulfide
γ-MnOOH	Manganite

# CHAPTER 1

## INTRODUCTION

### 1.1 Background

Foremost among the drivers of change is technology, spearheaded by the portable electronic technologies transformation which inevitably give rise to the rising demand for electrochemical energy storage (EES) devices. Therefore, a supercapattery was introduced as the latest energy storage device to combine the characteristic of a high energy lithium-ion batteries and a high-power supercapacitor (Yu & Chen, 2020b). However, there are still many challenges in developing supercapattery, including the method to incorporate of the cathodic and anodic materials to generate a high-performance EES device and the practical application of electrolytes with environmentally friendly and safer characteristics (Zhuang et al., 2019). The first goal of development a superior supercapattery systems is to ameliorate the electrochemical properties of the cathodic material.

In supercapattery, carbonaceous material from capacitive or pseudocapacitive materials is used as an anode, while battery-type materials such as  $\text{LiFePO}_4$  (LFP) (Shellikeri et al., 2018),  $\text{LiCoO}_2$  (LCO) (Lin et al., 2020),  $\text{LiNiO}_2$  (LNO) (Karuppiyah et al., 2020), and  $\text{LiMn}_2\text{O}_4$  (LMO) (Chen et al., 2018) as a cathode. Spinel LMO is a feasible and a greener cathodic material for supercapattery, which offer the benefit of low cost, eco-friendliness, good thermal stability, abundance reserves, and safer than the commercialized LCO (Lyu et al., 2021). In addition, the robust crystal structure of spinel LMO provides a stable framework, that fosters the lithium-ion diffusion channels and enables a low coulomb repulsion force and good thermal stability, thus resulting in high-rate capability (Marincaş & Ilea, 2021). Despite its advantages, LMO faced several challenges including poor electronic conductivity and low power density. Incorporation of LMO as cathodic material with carbon-based materials is one of an improvement approach to compensate for the low conductivity and improve the power and the energy density of LMO (Chen et al., 2019a). Several literature reported to fabricate a composite by integrated of LMO with graphene to ameliorate the power and energy density. Carbonaceous material such as graphene possesses the features of high specific surface area (SSA), electronic conductivity, and excellent mechanical flexibility is a promising carbon additives to generate a high efficiency supercapattery (Jia et al., 2011; Jung et al., 2013; Xu et al., 2012).

The studies on the effect of microstructure and surface chemistry of the LMO composite electrode have been researched extensively. Solid-state reaction method (SSR) synthesis is used extensively to synthesize LMO because of its process simplicity and is readily practiced on an industrial scale (Marincaş et al., 2020). LMO obtained by simple SSR reported by Kiani et al. successfully

delivered an exceptional specific capacity and proved a minimum of 75% capacity retention after verified by 100 cycling test (Kiani et al., 2011). Besides, the crystalline structure, morphology, and surface area of LMO is vital to dominate the performance in electric application as they influenced the electrochemical properties of LMO cathode material. LMO nanorods composed by a  $\beta$ -MnO<sub>2</sub> nanorods and the lithium hydroxide in an ethanol, accompanied by an annealing treatment provide better electrochemical characteristics, by retaining 86.2% of its initial capacity over 100 cycles (Chen et al., 2010). Nevertheless, the main disadvantages of SSR are poor electrode material crystallinity, uneven particle size, and high-energy utilization. This resulting in the determination of researchers to explore the efficient direction to synthesize LMO and its composite materials. Among the other investigated synthesis methods, the hydrothermal (HT) method is one of the most used synthesis routes which offers the advantages of better nucleation control, low energy consumption, high-purity compounds, and uniform particle distribution. Lv et al. have reported to synthesize a LMO cathode material with a high specific capacity and outstanding cycling stability via a single-step HT treatment at 120–180°C (Lv et al., 2014). Reduction on the particle size can be scrutinized at high synthesis temperature in HT method. An appropriate particle size of LMO promotes the electrochemical performance. However, the HT method required an expensive instrument of an autoclave reactor to produce a sufficient yield of LMO under controlled pressure and temperature.

It is crucial to develop and introduce an aqueous electrolyte in supercapattery application today by the reason of safety issue. The implementation of aqueous electrolytes in supercapattery is beneficial for the future applications in flexible, wearable, and portable electronic appliance. Considering the efforts taken until now, we took the challenge by developing an aqueous supercapattery device employing LMO-modified graphene nanoplatelets (LMO/GNPs) as cathode materials. Two synthesis methods of SSR and HT methods are chosen to fabricate the cathode materials. The physicochemical properties of synthesized materials are characterized and evaluated by different physicochemical techniques of X-ray diffraction (XRD), N<sub>2</sub> physisorption, and field emission scanning electron microscope (FESEM). Besides, the electrochemical performance of LMO/GNPs prepared by different synthesis methods is also investigated in the Swagelok cell configuration. The loading of 1 mg of GNP on LMO synthesized by the one-pot HT method (h-LMO/GNPs<sub>1</sub>) is found to deliver an exceptional specific capacitance of 329.36 F g<sup>-1</sup>, which is 1.6 and 1.7 times higher than pristine h-LMO and m-LMO/GNPs<sub>1</sub>, respectively. This is attributed to the smaller particle size and high surface area of the composite prepared via the HT method, and good electronic conductivity due to the presence of GNPs. Moreover, improved cycle stability of 82% capacity retention for over 1000 consecutive cycles is obtained with higher energy density and power density of 39.07 W h kg<sup>-1</sup> at 925.40 W kg<sup>-1</sup>, respectively, demonstrating its prospective electrode material for supercapattery.

## 1.2 Problem statements

Spinel LMO battery-type cathode material shows a great potential in real-life applications such as electric vehicles because of its low toxicity, low cost, the abundance of manganese elements, ease of synthesizing method, and high operating voltage ( $> 4.0V$ ) (Huang et al., 2021b; Marıncaş et al., 2020). Besides, it can achieve more than 90% of its theoretical capacity although it has a medium theoretical capacity of  $148 \text{ mA h g}^{-1}$  which is superior to the traditional lithium cobalt oxide (LCO) cathode material (Marıncaş et al., 2020). However, low conductivity and fast capacity fading after long cycling test limits their real-life application in practical (Chen et al., 2019a; Ji et al., 2022; Marıncaş et al., 2020; Zhang et al., 2021a). This limitation is associated with several factors such as Jahn-teller distortion and manganese dissolution. Besides, the crystal structure was transformed from cubic  $\text{LiMn}_2\text{O}_4$  to tetragonal  $\text{Li}_2\text{Mn}_2\text{O}_4$  attributable to the intercalation of lithium-ion. The phase transition reduced the lattice volume and destroyed the structural integrity of the LMO framework. Jahn-teller distortion associated with structural transformation hindered lithium-ion diffusion resulting in capacity deterioration (Xu et al., 2015). Manganese dissolution of  $\text{Mn}^{2+}$  ions caused by the disproportionation reaction of  $\text{Mn}^{3+}$  on the surface of the electrode ( $2\text{Mn}^{3+} \rightarrow \text{Mn}^{2+} + \text{Mn}^{4+}$ ) (Choi et al., 2015; Ji et al., 2022; Silva et al., 2022). Besides, polarization resistance may increase due to the deposition of dissolved  $\text{Mn}^{2+}$  onto the anode electrode as  $\text{MnO}$  or  $\text{Mn}$  metal, hence, capacity fading occurred by hindered  $\text{Li}^+$  diffusion and solid-electrolyte interface (SEI) film destruction (Chen et al., 2021a).

Element doping, surface coating and morphology and particle size modification are the strategies used to alleviate the limitation of LMO cathodic material in the energy storage devices (Silva et al., 2022). Element doping enhanced the structural stability of LMO, but it usually occurred at the expense of reduced initial specific capacity (Mu et al., 2019). Meanwhile, although surface coating alleviated the detrimental effects of spinel LMO, it reduced the intercalation rate of lithium-ion (Chen et al., 2019b). Thus, nanoscale particle size of LMO could mitigate the detrimental effects by modifying the ionic diffusion kinetics, the magnitude of stress-strain, surface energy, and the utilization of active material (Silva et al., 2022; Xia et al., 2012). Reduced particle size to strengthen the Mn-O bond and reduce the  $\text{MnO}_6$  framework improve structural stability to support  $\text{Li}^+$  diffusion during the continuous cycling process which restrains the Jahn-teller effect and Mn dissolution (Arabolla Rodríguez et al., 2021; Cai et al., 2015; Okubo et al., 2010). Moreover, hybridization of LMO with carbon matrix can compensate their low conductivity to promote electron transfer and ionic diffusion during the continuous charging and discharging process (Pyun & Park, 2015).

The electrochemical performances of supercapattery improved significantly by increasing the SSA, which can be controlled by different synthesis routes (Chen et al., 2019a; Lv et al., 2014). This approach enhanced the electron transport by creating a short  $\text{Li}^+$  diffusion length, increasing the electrode-electrolyte contact area, and improved the flexibility toward volume expansion ascribed to the lithium-ion insertion and desertion (Feng et al., 2015; Xia et al., 2012). Therefore,



heat treatment plays a critical parameter in the synthesis method to control the particle size as elevated temperature promoted rapid nucleation reaction and crystal growth, which is conducted in the formation of small particles size (Lv et al., 2014). The SSR was used to compare with the HT method which is widely used today to obtain the LMO/GNPs cathode materials with good electrochemical performance. The SSR was a traditional method used to synthesize LMO due to the ease of the synthesis process, and it applies to the large production scale, but it required a high heating temperature. In contrast, the synthesis method of HT is the facile and controllable particle size of products that can be obtained. Moreover, HT can be carried out at a lower temperature compared to SSR (Marincaş et al., 2020). Thus, two different synthesis methods were conducted to understand the intrinsic properties of LMO/GNPs obtained which affect their electrochemical performance.

### **1.3 Objectives**

The objectives of this study are:

1. To compare the electrochemical performance of lithium manganese oxide/graphene nanoplatelets composite synthesizing via the hydrothermal and solid-state reaction methods.
2. To optimize the graphene nanoplatelet contents in lithium manganese oxide/graphene nanoplatelets composite material.
3. To evaluate the power density and energy density of lithium manganese oxide/graphene nanoplatelets composite material in a two-electrode configuration of supercapattery device.



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