

**SYNTHESIS OF NASICON BASED  
( $\text{Na}_3\text{V}_{2-x}\text{Mo}_x(\text{PO}_4)_3/\text{C}$ ) AS HIGH CAPACITY AND  
STABLE CYCLING CATHODE MATERIALS  
FOR SODIUM-ION BATTERIES**

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**DOCTOR OF PHILOSOPHY  
(PHYSICS)**

**UNIVERSITI PERTAHANAN NASIONAL  
MALAYSIA**

**2021**



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Thesis submitted to the Centre for Graduate Studies, Universiti Pertahanan Nasional  
Malaysia, in fulfilment of the requirements for the Degree of Doctor of Philosophy  
(Physics)

## ABSTRACT

Sodium-ion batteries are techno-economically viable as a complement to the lithium-ion battery market segment. Among its kind, NASICON-structured  $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  offers improved  $\text{Na}^+$  insertion-extraction retention over high capacity, however, suffered from deterioration of cycle life and reduction of capacity retention. Establishment of the novel stoichiometric cathode by rejuvenating the interoperable parameters of calcination temperature and  $\text{Mo}^{6+}$  substitution on  $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  physicochemical performance is presented. Series of  $\text{Na}_3\text{V}_{2-x}\text{Mo}_x(\text{PO}_4)_3/\text{C}$  ( $0 \leq x \leq 1$ ) were synthesized by the self-catalysed sol-gel route have been investigated via experimental work and Density Functional Theory (DFT) simulation, to resolve these issues. Thermal Gravimetric Analyzer (TGA) designed optimum heat treatment procedure while X-ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), and Fourier Transform Infrared (FTIR) results confirmed the  $\text{Mo}^{6+}$  partial replacement on the  $\text{V}^{3+}$  site lattice resulting in significant electrochemical enhancement exhibited by Charge-Discharge (CD), Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) profile.  $\text{Na}_3\text{V}_{1.7}\text{Mo}_{0.3}(\text{PO}_4)_3/\text{C}$  demonstrates the highest specific capacity of  $122 \text{ mAh g}^{-1}$  at  $0.2\text{C}$  current rate. Two potential discharged plateaus are observed at  $3.4 \text{ V}$  and  $1.6 \text{ V}$  (vs.  $\text{Na}^+/\text{Na}$ ), corresponding to the  $\text{V}^{3+}/\text{V}^{4+}$  and  $\text{V}^{2+}/\text{V}^{3+}$  redox couple's activities respectively. Varied  $\text{Mo}^{6+}$  substitutions in  $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  crystalline structure indicate variations in d-spacing and lattice parameter values. Interestingly,  $\text{Na}_3\text{V}_1\text{Mo}_1(\text{PO}_4)_3/\text{C}$  corresponds to the highest  $\text{Mo}^{6+}$  concentration exhibits an extended voltage plateau in the low voltage region at  $1.6 \text{ V}$  which is promising as an anodic electrode for Na-ion batteries.

## ABSTRAK

Bateri ion-sodium secara tekno-ekonomi berdaya maju sebagai pelengkap segmen pasaran bateri ion-litium. Dikalangan jenisnya,  $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  berstruktur NASICON menawarkan daya kekal penyisipan-pengekstrakan  $\text{Na}^+$  yang lebih baik terhadap kapasiti tinggi, namun mengalami kemerosotan hayat kitaran dan pengurangan kapasiti kekal. Pembangunan stoikiometrik katod baru dengan menjajarkan semula parameter saling operasi suhu kalsinasi dan substitusi  $\text{Mo}^{6+}$  terhadap prestasi fizikokimia  $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  telah dibentangkan. Siri  $\text{Na}_3\text{V}_2-x\text{Mo}_x(\text{PO}_4)_3/\text{C}$  ( $0 \leq x \leq 1$ ) disintesis melalui proses sol-gel katalis spontan dikaji melalui eksperimental dan simulasi Teori Fungsi Kepadatan (DFT) untuk menguraikan permasalahan ini. Analisa Gravimetri Termal (TGA) merekabentuk prosedur rawatan haba optimum sementara Pembelauan X-ray (XRD), Spektroskopi Fotoelektron X-ray (XPS), dan Inframerah Transformasi Fourier (FTIR) mengesahkan substitusi  $\text{Mo}^{6+}$  terjadi pada kekisi  $\text{V}^{3+}$  menghasilkan peningkatan elektrokimia signifikan berdasarkan profil Cas-Nyahcas (CD), Voltammetri Kitaran (CV) dan Spektroskopi Impeden Elektrokimia (EIS).  $\text{Na}_3\text{V}_{1.7}\text{Mo}_{0.3}(\text{PO}_4)_3/\text{C}$  menunjukkan kapasiti spesifik tertinggi iaitu  $122 \text{ mAh g}^{-1}$  pada beban arus  $0.2 \text{ C}$ . Dua dataran voltan nyahcas diperhatikan pada  $3.4 \text{ V}$  dan  $1.6 \text{ V}$  (terhadap  $\text{Na}^+/\text{Na}$ ), menepati aktiviti pasangan redoks  $\text{V}^{3+}/\text{V}^{4+}$  dan  $\text{V}^{2+}/\text{V}^{3+}$ . Substitusi  $\text{Mo}^{6+}$  yang berbeza dalam struktur kristal  $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  menunjukkan variasi pada nilai parameter jarak-d dan parameter kekisi. Menariknya,  $\text{Na}_3\text{V}_1\text{Mo}_1(\text{PO}_4)_3/\text{C}$  yang berpadanan dengan kepekatan  $\text{Mo}^{6+}$  tertinggi memperlihatkan lanjutan dataran voltan di kawasan voltan rendah pada  $1.6 \text{ V}$  yang menjanjikan potensi sebagai elektrod anodik untuk bateri ion-sodium.

## ACKNOWLEDGEMENTS

First and foremost, praise and gratitude to Allah Almighty for blessing me far more than I deserve. Even though I stumbled along balancing working and dissertation battles for a long time, I'm grateful for the pain that taught me to appreciate this breakeven point of success.

Honorable mention for my main adviser, Lt. Kol. Prof. Ts. Dr. Muhd Zu Azhan bin Yahya, who engaged me in a precious educational process, instilled in me positive enthusiasm, and guided me for vast knowledge. A deep sense of thanks is also extended to Dr. Fadhlul Wafi bin Badruddin and Prof Madya Dr. Siti Aminah Binti Mohamad Noor for their huge help in scholarly guidance, scientific approach, and timely assistance in completing this dissertation process. Special thanks also acknowledge to the Faculty of Science and Defense Technology and Centre of Graduate Study, UPNM for facilitating matters throughout the learning curve.

My heartfelt appreciation also goes to my colleagues at Advanced Materials Research Centre, SIRIM Industrial Research, for their knowledge sharing and technical assistance throughout my research journey. Special thanks are also extended to the SIRIM Berhad management for their financial support and opportunity to pursue my Ph.D.

Last but not least, I would like to express my deepest gratitude and love to my family members, particularly my parent, Hj. Rosle Ahmad and Hj. Rohani Ibrahim, for their spiritual support and for always inspiring me throughout my life, and to my wife, Saidah Md Said, for all the sacrifices and patience she had to endure during my thesis preparation. You are all my driving force, and only God can repay all the good deeds done.

## APPROVAL

The Examination Committee has met on **16 November 2021** to conduct the final examination of **Mohamad Firdaus bin Rosle** on his degree thesis entitled '**Synthesis of NASICON Based ( $\text{Na}_3\text{V}_{2-x}\text{Mo}_x(\text{PO}_4)_3/\text{C}$ ) as High Capacity and Stable Cycling Cathode Materials for Sodium-ion Batteries.**

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## LIST OF ABBREVIATIONS

LIBs	-	Lithium-Ion Batteries
SIBs	-	Sodium-Ion Batteries
NASICON	-	Sodium Super Ionic Conductor
DFT	-	Density Functional Theory
CASTEP	-	Cambridge Serial Total Energy Package
BESS	-	Battery Energy Storage System
TGA	-	Thermo-Gravimetric Analysis
XRD	-	X-Ray Diffraction
BET	-	Brunauer-Emmet-Teller
FTIR	-	Fourier Transform Infrared
XPS	-	X-ray Photoelectron Spectroscopy
SEM	-	Scanning electron microscope
BJH	-	Barret-Joyner-Halenda
EDX	-	Energy-Dispersive X-ray
CD	-	Charge-Discharge
CV	-	Cyclic Voltammetry
DOS	-	Density of State
EIS	-	Electrochemical Impedance Spectroscopy
EEC	-	Equivalent Electrical Circuit
IUPAC	-	International Union of Pure and Applied Chemistry

## LIST OF SYMBOLS

$I$	- Current
$V$	- Voltage
$R_{el}$	- Electrolyte resistance
$R_{ct}$	- Charge transfer resistance
$R_{sl}$	- Surface layer resistance
CPE	- Capacitive constant phase element
$W$	- Warburg diffusion
$Q$	- Charge
$P$	- Pressure
$C$	- Current rate
$r$	- Radius
$X_m$	- Electronegativity value
$\theta$	- Incident angle
$d$	- Inter-planar spacing
$\lambda$	- Wavelength of X-ray
$E_{be}$	- Binding energy
$h\nu$	- Shift in photon energy
$\sigma$	- Warburg coefficient
$Z'$	- Real Impedance

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## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 Background**

The growing demand for high-capacity energy and power storage, fuelled by the urgent needs of contemporary electronic gadgets and the electric vehicle industry, has resulted in a recent surge in sales of rechargeable lithium-ion batteries. Since its commercial establishment in the early 1990s pioneering by Sony, rechargeable lithium-ion batteries have dominated the energy storage market under which had seized out the lead-acid, nickel-cadmium, and nickel-metal-hydrate as the previous nomination technology of choice. Lithium-ion batteries are notable for their large electrochemical potential, high gravimetric and volumetric energy density, low self-discharging rate, and excellent storage characteristic. Despite those significant key features, massive production of lithium-ion batteries had increased the global market anxiety towards the imminent exhaustion of lithium resources consequently to the arising of lithium precursor global price.

The new pace of change in large-scale smart grid technology developments remarkably required a large-scale energy storage system. Therefore, economic cost reduction and renewable resources are twofold concerns required to manage optimum